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Effects of Metal Ions on Viscosity of Aqueous Sodium Carboxylmethylcellulose Solution and Development of Dropping Ball Method on Viscosity

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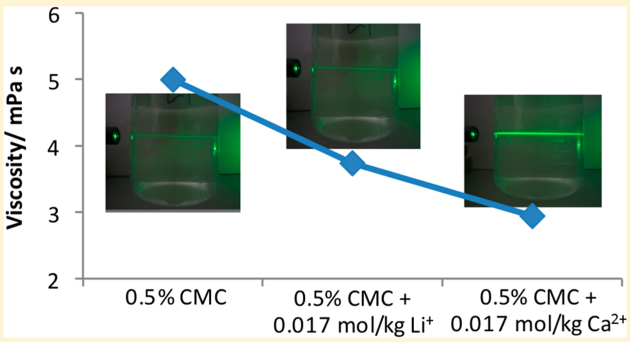
Supporting Information

ABSTRACT: This research revealed that metal ions with different charges could significantly affect the viscosity of aqueous sodium carboxylmethylcellulose (CMC) solution. On the basis of an Ostwald viscometer, an improvised apparatus using a dropping ball for examining the viscosity of liquids/solutions has been developed. The results indicate that the colloidal size of CMC aggregations is changed mainly by the metal cation charge. The improvised apparatus was introduced to high school students in a lesson on viscosity and intermolecular interaction where the students could examine the viscosity of several solutions and compare it with an aqueous sodium CMC solution. Although there are some limitations, the results show that the apparatus can be useful in helping high school students to understand the concept of viscosity.



KEYWORDS: *High School/Introductory Chemistry, First-Year Undergraduate/General, Laboratory Instruction, Physical Chemistry, Polymer Chemistry, Hands-On Learning/Manipulatives, Laboratory Equipment/Apparatus*

INTRODUCTION

Viscosity is an important and fundamental physical property of fluids as it is physically expressed in transportation phenomenon such as momentum of flow. Dynamic properties of solutions are commonly influenced by their static microscopic structures; however, these structures are difficult to deduce from their dynamic properties.

Sodium carboxylmethylcellulose (CMC) is a polymer substance popularly used in food and cosmetics, as well as in the agricultural, chemical and biological engineering fields due to its relatively high viscosity in aqueous solution and environmentally friendly nature.[1] Several researchers have investigated the properties of CMC and have published in this and other journals. Those studies have revealed the effectiveness of CMC as an additive, a substrate, a blending material, a stabilizer, a binder, a scaffold material, etc.[2−8]

In this study, we investigated the effects of several metal ions with different sizes and charges on the viscosity of aqueous CMC solution. In previous publications of this journal, there have been several reports introduced simple methods for classroom application to examine the viscosity of liquids, such as using a buret instead of Ostwald viscometer,[9] construction of an automated timing device for an Ostwald setup,[10] using an opto-mechanical mouse with the movement of a ball through the liquid by gravity,[11] and so on. Adapting from the previous research, this paper introduces a dropping ball method with simple and inexpensive apparatus, which was confirmed by an Ostwald viscometer. This paper also describes a classroom activity where the improvised apparatus was introduced to high school students in order to examine the effect of metal ions on viscosity of an aqueous CMC solution in a lesson on viscosity and intermolecular forces.

EXPERIMENTAL PROCEDURES

Preparation of Sample Solutions

CMC as sodium salt with average molecular weight of ca. 90 000 (purchased from ACROS ORGANICS) was used in this study. Each metal salt; LiCl, NaCl, KCl, $CaCl_2$, $AlCl_3$ and $[Co(NH_3)_6]Cl_3$ was dissolved in 0.50% (w/v) aqueous CMC solution in the range 0.00−0.10 mol kg^{-1}. The concentration of 0.50% (w/v) aqueous CMC solution is suitable for an Ostwald viscometer with 1.0 mm capillary diameter. Lower concentrations show only small changes of viscosity with different metal ions, while higher concentrations have difficulty flowing through the Ostwald capillary as they are too viscous.

Ostwald Viscometer

The precise viscosity value of each sample was obtained by using an Ostwald viscometer (capillary diameter = 1.0 mm) relative to the standard value of distilled water as solvent. A 10

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mL sample was placed into the viscometer, immersed in a water bath at 25 °C (±0.01 °C) and kept for 2 min to stabilize the temperature. The sample was drawn by suction into the smaller reservoir of the viscometer and then allowed to flow by gravity. The flow time of the sample along the capillary from the upper to the lower mark on the viscometer was recorded. Five repetitions were measured for each sample (maximum deviation from the mean was ±0.10 s) and an average was obtained. The viscometer was washed between samples with a portion of the next sample to be measured. The viscosity of the sample was then calculated from the following equation which was derived from the Poiseuille equation

$$\frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0 t_0}$$

Where η_0/mPa s, ρ_0/g cm^{-3}, t_0/s, η/mPa s, ρ/g cm^{-3}, t/s are viscosity, density, and flow time of water and aqueous sample, respectively. The standard values of viscosity (η_0) and density (ρ_0) for water at 25 °C were taken from the literature,[12] while the densities of samples were measured by the pycnometer method.

Development of Dropping Ball Method

In the procedures developed, a transparent plastic tube having 2 cm inner-diameter and 1 m length was installed vertically on a stand with the bottom end of the tube closed by a rubber stopper. The tube was marked with two lines 500 mm apart. A volume of 250 mL of the sample solution was placed into the tube at room temperature and kept for a minute to allow the solution to stabilize. Plastic balls from a toy gun were used as dropping balls with the density of 1.020 g/cm^3 and dropped into the sample solution at the top of the tube. The time for the ball to fall from the upper to the lower line on the tube by gravity was recorded. Five replicate measurements were collected with five balls, and the three middle measurements were chosen for calculation of the average time. The maximum deviation from the mean was less than ±1 s. Finally, the speed of the dropping ball in each sample was obtained. All measurements were conducted at room temperature (ca. 25 °C). The same number of measurements were carried out with the Ostwald viscometer at 25 °C as mentioned above and used for calibration.

■ HAZARDS

No dangerous chemical or procedure was employed in this experiment.

■ RESULTS AND DISCUSSION

Ostwald Viscometer

Figure 1 shows that metal ions have significant effects on the viscosity of aqueous 0.50%w/v CMC solutions and its extent is particularly dependent on metal ion charges. The cation size effects of 1+ metal ions such as Li^+, Na^+, and K^+ on viscosity are all very similar. The viscosity of the aqueous CMC solutions gradually decreases with the increase of alkali metal chloride concentration. On the other hand, the effect of calcium ion with 2+ charge is more dramatic. The CMC viscosity decreases much more quickly with the increase of $CaCl_2$ concentration. However, in the case of 3+ cations such as Al^{3+} and $[Co(NH_3)_6]^{3+}$, the rapid formation of precipitates with the CMC anion occurred as white ($[Al_m(CMC)_n]$) and orange

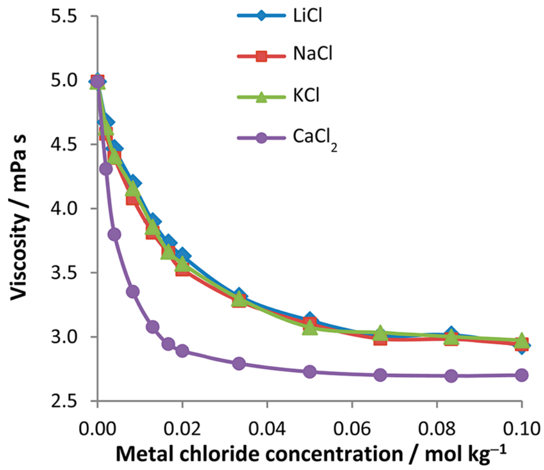

Figure 1. Effects of metal ions on viscosity of aqueous 0.50% (w/v) CMC solution at 25 °C.

$\{[Co(NH_3)_6]_p(CMC)_q\}$. Therefore, the results for 3+ cations are not shown in Figure 1.

The results suggest that in 0.50% CMC(aq) without the addition of alkali salt, CMC anions are dispersed because of electrostatic repulsion. So, the aqueous CMC solution shows a relatively high viscosity caused by the dispersed long CMC polymer chains. The addition of the excess alkali cations into the CMC solutions can cause aggregation between CMC anions and metal ions due to cancelation of the electrostatic repulsion. This aggregation phenomenon reduces the number of free CMC anions and reduces the viscosity. The Ca^{2+} cations can attract more CMC molecules to form bigger colloidal particles, thus reducing the viscosity further. The aggregation of colloidal particles can be identified clearly by Tyndall effect, where the solutions of CMC with 1+ metal ions show similar Tyndall phenomena more clearly than that of CMC alone. This phenomenon is even more pronounced with 2+ metal ion (Ca^{2+}). *The Tyndall effect and diagrams of CMC molecule aggregation are included in the Supporting Information cocument.*

Dropping Ball Method

In general, the faster dropping speed indicates the lower viscosity. In our results, the dropping speeds are increased almost proportionally with metal chloride concentration or inversely to the solution viscosity by Ostwald method, but only within a small concentration range. When the metal chloride amounts are increased more than a certain concentration, the dropping speed gradually decreases for the investigated alkali metal chloride, and drastically for $CaCl_2$. As shown in Figure 2, the dropping speeds are varied almost inversely as the solution viscosity increases. However, the dropping speeds are decreased dramatically when the metal chloride concentrations are increased over 0.050 mol kg^{-1} for LiCl, 0.033 mol kg^{-1} for NaCl and KCl, and 0.017 mol kg^{-1} for $CaCl_2$, while the viscosities of solutions are almost same from these concentrations. This is due to the buoyancy effect on the ball dropping speed, caused by the increase of the sample density resulting from the addition of metal chloride. As the results, the dropping speed is getting decrease drastically, when the density of the sample is increasing closer to the density of the dropping ball.

Therefore, using the dropping method to estimate viscosity of the sample solutions in this research seems to be only applicable for CMC solutions within a certain concentrations of metal ions or metal salts. Another limitation of the dropping

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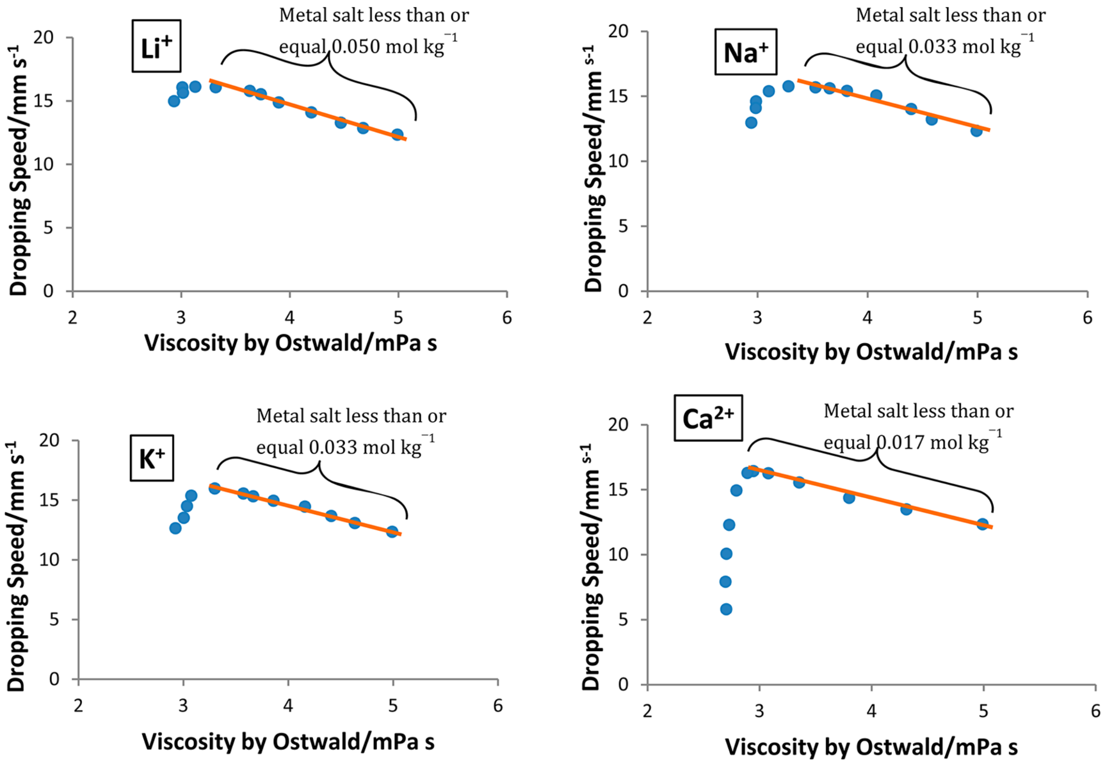

Figure 2. Relationship of dropping speed with viscosity at 25 °C.

ball method is the difficulty of measurement at temperatures other than room temperature. One suggestion for improvement of this improvised apparatus is the use of a denser ball instead of a plastic ball (d = 1.020) to measure viscosity at higher metal ion concentrations.

■ APPLICATION TO CLASSROOM

We introduced the dropping method to high school students at tenth grade in Japan through lessons on viscosity and intermolecular interaction, in July 2014 based on the findings of this research. In the lessons, the students investigated and compared the different viscosities of distilled water, 0.50% NaCl(aq), 0.50% CMC(aq), 0.017 mol kg^{-1} NaCl(aq) in 0.50%CMC(aq) and 0.017 mol kg^{-1} $CaCl_2$(aq) in 0.50% CMC(aq). Two lab periods of 50 min were used to complete all of the activities. The students needed approximately 25 min to conduct experiments as a group in each period. In the first period after 5 min prelesson assessment, the instructor helped students to explore some basic concept about viscosity of liquids and its daily application. Several questions were asked to engage the students such as, "What does viscosity mean?", and "How do metal ions affect viscosity of CMC solution?", etc. By following the worksheet, the students were asked to formulate an hypothesize and then investigate how viscosity differed between water, 0.50%NaCl(aq) and 0.50%CMC(aq). In the second period, the students continued formulating their hypothesis and investigating the viscosity of 0.017 mol kg^{-1} NaCl(aq) in 0.50%CMC(aq) and 0.017 mol kg^{-1} $CaCl_2$(aq) in 0.50%CMC(aq). In the last 30 min, the students discussed as a group then drew a bar chart of the average dropping speeds of the plastic gun ball through each sample solution. The 0.50% CMC(aq) and materials were prepared for the students before the class periods, while adding the metal salts into water and 0.50% CMC(aq) to make the mixture samples were made by the students in the class. The students' results from a representative group are shown in Figure 3. At the end of the lessons, the students were able to discuss and explain the effects of metal ions on the viscosity of CMC(aq) by using the molecular or particle structure diagrams. Finally, the lesson contents were summarized and the Tyndall Effect briefly demonstrated by the instructor. *The student handout, worksheets and lesson plan for the teacher are available in the* Supporting Information.

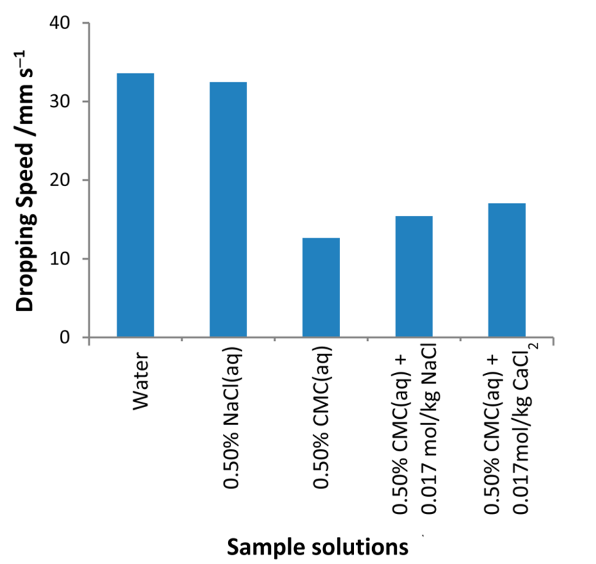

Figure 3. Students' results on investigation of the sample solution viscosities by the dropping ball method.

It was interesting that after introducing diagrams of molecular structures of CMC to be investigated, the students

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could effectively formulate their hypothesis on the worksheets and could hardly wait to conduct the experiments to confirm their hypothesis. During the investigation, the students were surprised that the presence of metal salts decreased the viscosity of aqueous CMC solution, because most of them thought that adding more substances into a solution would make the viscosity increase. The presence of the metal cations can screen the charges on the CMC, thereby causing the polymer chains to shrink corresponding to the decrease in viscosity. While the viscosity of water was confirmed to be similar to that of NaCl(aq), and CMC(aq) had the highest viscosity among the investigations based on the experimental results, the students also found out that $CaCl_2$ decreased the viscosity of CMC(aq) more than NaCl.

From the students' group discussion and after the final lesson summary by the instructor, the students could well understand that the aggregations of CMC molecules and metal ions could change the viscosity of a solution. Therefore, in addition to introducing sizes and shapes of particles, the lessons provided students with an opportunity to learn about intermolecular interaction, which is another factor that affects the viscosity of solutions. The intermolecular forces involved in this system include hydrogen bonding among CMC molecules and electrostatic interaction (among CMC molecules and metal cations) in aqueous solution.[13] At the end of the lesson, the students received additional explanation about the limitations of the dropping ball method caused by the buoyancy effect as discussed in Figure 2.

■ CONCLUSION

The study revealed that metal ions at low concentrations could decrease the viscosity of an aqueous CMC solution. Especially, by using the dropping ball method with improvised apparatus described here, students could examine and compare the viscosities of solutions and discuss intermolecular force in the classroom.

Although the dropping ball method has some limitations, such as consuming greater amounts of solution, temperature not easily controllable and providing only a relative not a real viscosity value, we hope that the associated ideas will be valuable in the instruction of basic chemistry, especially in situations which lack experimental apparatus. Therefore, as an addition to other student-made instruments, this improvised apparatus can be recommended for examining the viscosity of liquids or solutions, as well as being an effective teaching material for high school chemistry classes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A detailed discussion of the contents, handouts for students and lesson plans. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Hollabaugh, C. B.; Burt, L. H.; Walsh, A. P. Carboxymethylcellulose: Uses and Applications. *Ind. Eng. Chem.* **1945**, *37* (10), 943−947.

(2) Li, J.; Li, Y.; Dong, H. Controlled Release of Herbicide Acetoclor from Clay; Carboxylmethylcellulose Gel Formulations. *J. Agric. Food Chem.* **2008**, *56*, 13336−1342.

(3) Su, F. J.; Huang, Z.; Yuan, Y. X.; Wang, Y. X.; Li, M. Structure and properties of carboxymethyl cellulose/soy protein isolate bland edible films cross linked by Maillardreactions. *Carbohydr. Polym.* **2010**, *79*, 145−153.

(4) Cheng, C. K.; Catchmark, M. J.; Demirci, A. Effects of CMC Addition on bacterial cellulose production in a Biofilm Reactor and Its Paper Sheets Analysis. *Biomacromolecules* **2011**, *12*, 730−736.

(5) Sengupta, S.; Jana, M. L.; Sengupta, D.; Naskar, A. K. A note on the estimation of microbial glycosidase activities by dinitrosalicylic acid reagent. *Appl. Microbiol. Biotechnol.* **2000**, *53*, 732−735.

(6) Li, J.; Lewis, R. B.; Dahn, J. R. Sodium Carboxymethyl Cellulose A Potential Binder for Si Negative Electrodes for Li-Ion Batteries. *Electrochem. Solid-State Lett.* **2007**, *10* (2), A17−A20.

(7) Hicyilmaz, C.; Ozun, S.; Altun, E. N. Rheological Properties of Asphaltite-Water Slurries. *Energy Fuels.* **2006**, *20*, 2037−2045.

(8) Tang, Y. L.; Zhou, Z. J.; Ogawa, K.; Lopez, G. P.; Schanze, K. S.; Whitten, D. G. Sythesis, Self-Assembly, and Photo-physical Behavior of Oligo Phenylene Ethylylenes: From Molecular to Supra-molecular Properties. *Langmuir* **2009**, *25*, 21−25.

(9) Sorrell, A. C. Liquid Viscosity Measurement Using a Buret. *J. Chem. Educ.* **1971**, *48* (4), 252−254.

(10) Urian, R. C.; Lutfur, R. K. A Diode-Laser Based Automated Timing Interface for Rapid Measurement of Liquid Viscosity. *J. Chem. Educ.* **1998**, *75* (9), 1135.

(11) Mohammad, M. D.; Norooz, M.; Hojjatollah, K. A Low-Cost Viscometer from an Opto-mechanical Mouse. *J. Chem. Educ.* **2010**, *87* (12), 1411−1413.

(12) Weast, C. B.; Astle, J. M.; Beyer, H. W. *CRC Handbook of Chemistry and Physics*, 69th ed.; RCR Press, Inc., Boca Roton, FL, 1988−1989; pp F-4 and F-40.

(13) Yang, X. H.; Zhu, W. L. Viscosity properties of sodium carboxymethylcellulose solutions. *Cellulose* **2007**, *14* (5), 409−417.

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J. Chem. Educ. 2015, 92, 946−949