Study on the Method of Measuring the Molecular Weight of Polycarboxylate Water Reducer by Gel Chromatography

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Abstract. The effects of the type of mobile phase and its flow rate, column temperature, and detector temperature on the chromatographic peak separation and molecular weight test results of polycarboxylate water-reducer were studied. A method for measuring the molecular weight of polycarboxylic acid water-reducing agent by gel chromatography was established, and the accuracy of the method was verified by using two dextran standard substances of standard sample 2, standard sample 3. The results show that a 0.1 mol/L sodium nitrate solution containing 0.05% sodium azide should be selected as the mobile phase, the flow rate is 0.8-0.9 mL/min, and the column temperature and the detector temperature are 35-40 ℃. It has been verified that the relative errors of the molecular weight test results of standard sample 2 and standard sample 3 are all less than 5%, and the MP, Mn, and Mw values measured by this measurement method are close to the true values.

1. Introduction
Polycarboxylic acid type water reducer (PCE), as the third generation superplasticizer (SPs), is regarded as an important additive in modern cement technology [1]. The performance of polycarboxylic acid water-reducing agent not only depends on the raw materials used, but also related to the weight-average molecular weight and relative molecular weight distribution of the water-reducing agent [2]. Therefore, it is necessary to analyze and control the molecular weight of polycarboxylic acid water reducing agent when synthesizing polycarboxylic acid water reducing agent [3]. Methods for measuring the molecular weight of polymers include: vapor osmotic pressure method (VPO), membrane osmotic pressure method, viscosity method, light scattering method and GPC method [4]. Among them, gel chromatography is recognized as an effective method for molecular weight determination. It can not only determine the molecular weight value, but also obtain the molecular weight distribution. This method has first been widely used in the biological and pharmaceutical fields [5]. In recent decades, gel chromatography technology has gradually developed in environmental monitoring and plastic manufacturing. Regarding the molecular weight test of polycarboxylic acid water-reducing agents, although relevant literature has reported, there is no specific and uniform test method for the molecular weight testing of different types of polycarboxylic acid water-reducing agents.

In this paper, dextran whose molecular weight is similar to that of polycarboxylic acid water reducer is selected as the standard substance. By investigating the influence of the type of mobile phase and its flow rate, column temperature, and detector temperature on the chromatographic separation of polycarboxylate water-reducing agent and the molecular weight test results, the best test
conditions were determined. A standard curve was established and a new method for molecular weight testing of polycarboxylic acid-based high-performance water-reducing agents was developed.

2. Experiment

2.1. Materials and equipment
S08F (KZJ New Materials Group Co. Ltd), S10E-G180286 (KZJ New Materials Group Co. Ltd), dextran standard substance, sodium azide (analytically pure), sodium nitrate (analytically pure), ultrapure water, methanol (analytically pure), buffer solution (containing 38.6mmol/L NaCl and 10.0mmol/L NaH2PO4).

Gel permeation chromatograph, chromatographic column (UltrahydrageTM water-soluble gel column, Ultrahydrogel 250 and Ultrahydrogel 500 of two different types of chromatographic columns in series, with a wide pH range of 2-12), analytical balance, ultrasonic cleaner, suction filter device, column thermostat, differential detector.

2.2. Experimental conditions
Mobile phase A (ultra-pure water), mobile phase B (0.1 mol/L sodium nitrate solution containing 0.05% sodium azide), mobile phase C (methanol + buffer solution (containing 38.6 mmol/L NaCl and 10.0 mmol/L NaH2PO4), Volume ratio 75:25), the detector temperature range is 30-50 ℃, the detector sensitivity is 8, the detection wavelength is 220 nm, and the quantitative loop capacity is 200μL.

2.3. Solution preparation
2.3.1. Preparation of mobile phase.
The newly prepared ultrapure water was ultrasonically degassed with an ultrasonic instrument for 30 minutes to obtain mobile phase A. Weigh 0.5g of sodium azide and 8.5g of sodium nitrate, dissolve it with freshly prepared ultrapure water, transfer it to a 1L volumetric flask, shake it up after constant volume, and use a vacuum filtration device for suction filtration (containing 0.45 Micron water-based filter membrane), ultrasonic degassing for 30 minutes to obtain mobile phase B. After mixing methanol and buffer solution (containing 38.6mmol/L NaCl and 10.0mmol/L NaH2PO4) at a volume ratio of 75:25 and filtering, the mobile phase C was obtained by ultrasonic degassing with an ultrasonic instrument for 30 minutes.

2.3.2. Preparation of sample solution.
Weigh the calculated mass of the sample, dissolve the sample with mobile phase, and leave it for a period of time after proper stirring to make the sample completely dissolved.

3. Results and discussion
3.1. Mobile phase selection
Prepare different mobile phase solutions, randomly select two polycarboxylic acid mother liquors S08F and S10E-G180286 as samples, and each sample was tested twice in parallel under different mobile phase conditions. The flow rate of the fixed instrument was 8mL/min, the temperature was 40℃, and the detector sensitivity was 8, and the separation effect of the mobile phase was investigated. The baseline monitoring equilibration time of different mobile phases and the sample information were shown in Table 1, and the chromatographic peak separation of samples under different mobile phase conditions were shown in Figure 1 and Figure 2.

It can be seen from Table 1 that the pH of mobile phase A, mobile phase B and mobile phase C are 6.96, 6.61, and 7.27 respectively, which are in line with the pH range of the chromatographic column (pH=2-12). Mobile phase C has not reached equilibrium after 4 hours of baseline monitoring, while the baseline equilibrium time of mobile phase A and mobile phase B is about 1.5 hours. After
chromatogram comparison analysis, under the same conditions, the mobile phase A has an unsatisfactory effect on the sample peak separation of S08F and S10E-G180286 samples, while the mobile phase B can separate the samples well. Therefore, mobile phase B is selected as the mobile phase for the method research of this project.

Table 1. Sample information and baseline monitoring equilibration time of different mobile phases.

| Serial number | Sample      | Mobile phase | pH    | Time/h |
|---------------|-------------|--------------|-------|--------|
| 1             | S08F        | A            | 6.96  | 1.5    |
| 2             | S08F        | A            | 6.96  | 1.5    |
| 3             | S10E-G180286| A            | 6.96  | 1.5    |
| 4             | S10E-G180286| A            | 6.96  | 1.5    |
| 5             | S08F        | B            | 6.61  | 1.5    |
| 6             | S08F        | B            | 6.61  | 1.5    |
| 7             | S10E-G180286| B            | 6.61  | 1.5    |
| 8             | S10E-G180286| B            | 6.61  | 1.5    |
| 9             | /           | C            | 7.27  | >4     |

3.2. Velocity of mobile phase

When the column temperature is 40℃ and the sensitivity is 8, the S08F, the S10E-G180286, the standard material 2 and the standard material 3 were used to verify the separation effect of chromatographic peaks at flow rates of 0.7, 0.8, 0.9 and 1.0 mL/min respectively. The peak separation is shown in Figure 3 to Figure 6. The Standard material 2 and the standard material 3 were used to verify the molecular weight test results, and each sample was tested 3 times in parallel. On the basis that the relative standard deviation of the 3 parallel molecular weight measurement results is less than 5%, take the average of the 3 measurement results and compare and analyze with the molecular weight reference value of the standard sample. Figure 7 shows the relative error between the average of the three measurement results and the reference value under different flow rates.

From Figure 3 to Figure 6, it can be seen that the solute peaks and solvent peaks of the four samples can be separated well when the flow rates are 0.7mL/min, 0.8mL/min, 0.9mL/min and 1.0mL/min. And S08F, S10E-G180286 polymer peak and monomer peak separation effect is good. It can be seen from Figure 7 that when the flow rate is 0.7 mL/min, the relative error of the test result of the number average molecular weight Mn of the standard sample 3-21400 is 7%, which is larger than
other measurement results, and when the mobile phase flow rate is 0.7 mL/min, a single time The injection run time is longer. Therefore, the more appropriate mobile phase velocity is 0.8-1.0 mL/min. To prevent excessive flow rate from damaging the instrument, the recommended flow rate is 0.8-0.9 mL/min.

Figure 3. Chromatographic peak separation effect at a flow rate of 0.7 mL/min.

Figure 4. Chromatographic peak separation effect at a flow rate of 0.8 mL/min.

Figure 5. Chromatographic peak separation effect at a flow rate of 0.9 mL/min.

Figure 6. Chromatographic peak separation effect at a flow rate of 1.0 mL/min.

Figure 7. Relative error of measurement results under different flow rate conditions.
3.3. Column temperature and detector temperature

When the sensitivity was 8 and the flow rate was 0.8 mL/min, 4 samples of S08F, S10E-G180286 and standard material 2 and standard material 3 were used under the conditions of chromatographic column and detector temperature of 30, 35, 40 and 45°C respectively. Verify the chromatographic peak separation effect, see Figure 8 to Figure 11 for the chromatographic peak separation situation. Standard substance 2 and standard substance 3 were used to verify the molecular weight test results, and on the basis of the relative standard deviation of the three parallel molecular weight measurements <5%, the average of the three measurements was taken. Compare and analyze the average of the three measurement results with the molecular weight reference value of the standard sample, the relative error of the measurement results under different temperature conditions were shown in Figure 12.

It can be seen from Figure 8 to Figure 11 that the solvent peak and the solute peak can be completely separated at the column temperature of 30, 35, 40 and 45°C, and the polymer and small molecules also have a good separation effect. It can be seen from Figure 12 that under different temperature conditions, among the molecular weights tested with standard sample 2 and standard sample 3, the largest relative error from the reference value is the MP value of standard sample 3-21400 measured at 45°C. The error value is 5.96%. The second is the MP value of the standard sample 3-21400 measured at 30°C, the error value is 5.74%. In order to reduce the measurement error, the recommended measurement temperature range is 35 - 40°C.

Figure 8. Chromatographic peak separation effect at 30°C.
Figure 9. Chromatographic peak separation effect at 35°C.
Figure 10. Chromatographic peak separation effect at 40°C.
Figure 11. Chromatographic peak separation effect at 45°C.
3.4. Establishment of standard curve and method verification
Select mobile phase B as the best mobile phase. Under the conditions of a flow rate of 0.8 mL/min, a temperature of 40°C, and a sensitivity of 8, establish a standard curve, as shown in Figure 13, and create a related data processing method. On this basis, standard sample 2 and standard sample 3 were used to investigate the measurement error. Each sample was tested twice in parallel, and the test results were shown in Table 2.

It can be seen from Figure 13 that each point in the figure falls on the curve, $R^2=0.999791$, indicating that the standard curve fitting effect is very good. It can be seen from Table 2 that the relative errors of the test results of standard sample 2 and standard sample 3 are all less than 5%, and the MP, Mn, and Mw values measured by this measurement method are close to the true values.

| Serial number | Standard sample | Reference Measurements | Relative error (%) |
|---------------|----------------|------------------------|--------------------|
|               | MP  | Mn  | Mw  | MP  | Mn  | Mw  | MP  | Mn  | Mw  |   |
| 1             | 3   | 21400 | 18300 | 23800 | 22022 | 18063 | 23102 | 2.91 | 1.30 | 2.93 |
| 2             | 3   | 21400 | 18300 | 23800 | 22076 | 17903 | 23000 | 3.16 | 2.17 | 3.36 |
| 3             | 2   | 9900  | 8100  | 11600 | 9670  | 7802  | 11199 | 2.32 | 3.68 | 3.46 |
| 4             | 2   | 9900  | 8100  | 11600 | 9665  | 7907  | 11305 | 2.37 | 2.38 | 2.54 |
4. Conclusions
The results of the study on the determination of the molecular weight of polycarboxylate superplasticizer by gel chromatography show that the appropriate mobile phase is 0.1 mol/L sodium nitrate solution containing 0.05% sodium azide, and the recommended flow rate is 0.8-0.9 mL/min. The recommended column temperature and detector temperature are 35-40°C. Standard sample 2 and standard sample 3 were used to verify the established measurement method and found that the relative error between the test results of the two samples and the reference value was less than 5%. The MP, Mn, and Mw values measured by this measurement method are close to the real values, and the measurement error is small.

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