Measurement of the coordination effect of polyphenols used in oil field by colorimetric method

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Abstract. Polyphenols are widely used in drilling fluid, cement slurry and water treatment in oil fields. The paper is based on the characteristics of the abundant phenolic hydroxyl groups in plant polyphenol compounds that can form stable complexes with iron ions, and the characteristics of phenolic compounds forming blue-violet to brown complexes with iron salts, and the color of iron salts itself for light yellow, a color method is designed to evaluate the quality of polyphenols, which provides a simple and reliable method for the quality analysis of industrial polyphenols.

Keywords: Phenolic compounds; quantitative analysis; coordination; colorimetric

1 Introduction

Polyphenols are a kind of renewable energy with wide distribution, variety and large quantity. Its rich phenolic hydroxyl groups give it a series of unique chemical properties, which not only have the effect of reducing viscosity and fluid loss in drilling fluids, but also have a certain anti-collapse effect [1,2]. Polyphenol compounds can form a protective film on the surface of steel to prevent further corrosion, so these compounds also have a certain corrosion inhibition [3,4]. It is precisely because of its rich phenolic hydroxyl structure that polyphenol compounds can react with high-valent ions such as iron ions and aluminum ions to form stable complexes [5], thereby forming a protective film to prevent steel corrosion. However, the ortho-para phenolic hydroxyl group in the phenolic hydroxyl structure of plant phenols is easy to be oxidized to quinone structure, resulting in the decline of its coordination ability [1]. Based on the characteristics of phenolic compounds forming blue-violet to brown complexes with iron ions, the color of iron ions themselves is light yellow. When iron ions are gradually added, the color of the mixed solution system gradually darkens (the absorbance increases). When the ion reaches the saturation coordination, its increase will be significantly weaker, that is, an inflection point is generated [6-8]. From this inflection point, the amount of coordinated phenolic hydroxyl provided by plant phenols can be calculated according to the conventional coordination form of phenolic hydroxyl and trivalent iron ion 6:1. Therefore, the absorbance change of the complex

formed with iron salt is used to evaluate the effective phenolic hydroxyl content in plant phenolic materials, and as an index to evaluate their quality.

2 Experimental

2.1 Materials

FeCl₃ was purchased from Tianjin Komiou Chemical Reagent Co., Ltd. Phenol was supplied from Zhengzhou Zhongtian Experimental Instrument Co., Ltd. Hydroquinone was purchased from Tianjin Third Chemical Reagent Factory. Phloroglucinol was purchased from Ouhai Chemical Reagent Factory in Wenzhou City, Zhejiang Province. Tannin was purchased from Yancheng Ourui International Trade Co., Ltd. Sodium Lignosulfonate was purchased from Beijing Jiahemu Technology Co., Ltd. Alkali lignin was purchased from Luohe East China Lignin Co., Ltd.

2.2 Method

In this experiment, for monophenols, first prepare 50ml of the same molar concentration of ferric chloride solution and polyphenols solution in a volumetric flask, and then take 10ml volumetric flasks, numbered 1# to 10#. Add 3ml phenol solution into 10 volumetric flasks in sequence, and add 0 ml, 0.3ml, 0.35ml, 0.4ml, 0.45ml, 0.5ml, 0.6ml, 0.75ml, 1ml and 1.5ml ferric chloride solution in sequence. Fix the volume with industrial ethanol and

measure its absorbance at 510nm (the maximum absorption wavelength of ferric iron). If the absorbance value is between 0.2-0.7, the measured data is valid, The best coordination ratio can be obtained by fitting two straight lines from the scatter trend diagram and finding the intersection point. For bisphenols and triphenols, using the same method, the volume of ferric chloride solution increases the corresponding multiple of phenolic hydroxyl group under other conditions. or gallic acid and tannic acid with known molecular weight, prepare a solution with appropriate molar concentration according to the previously known trend line of polyphenols, draw a similar trend line, and then calculate the best ratio of the substance. For sodium lignosulfonate and alkali lignin with unknown molecular weight, use the solution with the same mass concentration as ferric chloride and adopt the above method, Draw two straight lines to calculate the trivalent iron ion equivalent, that is, the mass of alkali lignin that can effectively coordinate with each gram of ferric chloride, which has achieved the purpose of quantitative analysis.

3 Results and discussion

3.1 Mechanism study

At the wavelength of 510 nm, different absorbance values were obtained after the color development of ferric chloride and fixed concentration phenol in different ratios. The molar ratio of ferric ion to phenolic compounds was taken as the X axis and the corresponding absorbance was taken as the Y axis. In certain range, iron ions coordinate with phenolic hydroxyl groups of phenols, the absorbance increases with the increase of iron ion concentration, and the color of the solution system gradually deepens [9]. After exceeding a certain concentration, because there is no coordinated phenolic hydroxyl group, continue to increase the concentration of iron ion, the increase range of absorbance of the system becomes weak, and only the color of iron ion itself is increased [10]. Calculate the linear relationship between the two intervals. The X value at the intersection is the best coordination molar ratio between phenols and ferric ions, and the concentration of iron ions (C_{Fe} , mol/L) can be found here. The ratio of the concentration to the phenol concentration (C_p , g/L) is multiplied by the coefficient of iron ion saturation coordination 6, to obtain the coordination index M , $M=(C_{Fe}/C_p) \times 6$ (mol/g). In this experiment, products with high purity, such as chemical pure and analytical pure products, are used as control experiments to obtain their coordination index and compare it with that of industrial products. The closer they are, the higher the quality is, so their quality can be evaluated [11].

3.2 Coordination of monophenol with ferric chloride

The color development of phenol and ferric ions is shown in Figure 1. It can be seen from the figure that the intersection value is $X=0.19$, $Y=0.49$, that is the molar

ratio of ferric chloride to phenol is 0.19, and the same molar ratio of phenol to ferric chloride is 5.4. In a word, when the molar ratio to ferric chloride is 5.4, it is the effective coordination ratio.

Fig. 1 Relationship between molar ratio of ferric chloride to phenol and absorbance

3.3 Coordination of bisphenol with ferric ion

The color development of hydroquinone and iron ion is shown in Figure 2. It can be seen that the intersection value is $x = 0.36$ and $y = 0.41$, the molar ratio of ferric chloride to hydroquinone is 0.36 and the molar ratio of hydroquinone to ferric chloride is 2.8. In other words, when the molar ratio of hydroquinone to ferric chloride is 2.8, a saturated coordination ratio is formed, indicating that it is difficult for both hydroxyl groups in the molecule to participate in coordination.

Fig. 2 Relationship between molar ratio of ferric chloride to hydroquinone and absorbance

3.4 Coordination of triphenol with ferric ion

The color development of phloroglucinol and iron ion is shown in Figure 3. The intersection point can be seen from the figure: $x = 0.54$, $y = 0.36$, that is when the molar ratio of ferric chloride to phloroglucinol is 0.54 or the molar ratio of phloroglucinol to ferric chloride is 1.8, that is, when the molar ratio of phloroglucinol to ferric chloride is 1.846, an effective coordination ratio is formed and close to the theoretical value of 1:2, indicating that the

three hydroxyl groups in the molecule are difficult to participate in coordination.

Fig. 3 Relationship between molar ratio of ferric chloride to phloroglucinol and absorbance

3.5 Evaluation of coordination ability of polyphenol materials with unknown quality

Based on the above research, industrial tannic acid is used for coordination reaction with iron ions. From Fig. 4, it can be seen that the coordinates of the intersection point are: $x=2.23$, $y=0.32$, that is the molar ratio of ferric chloride to tannic acid is 2.23. The value shows that 6 mol of phenolic hydroxyl and 1 mol of ferric chloride are effectively coordinated. Therefore, the phenolic hydroxyl group that can effectively coordinate with ferric ion in 1 mol tannic acid is $2.23 \times 6=13.4$ mol.

Fig. 4 Relationship between molar ratio of ferric chloride to tannic acid and absorbance

Industrial sodium lignosulfonate is used to coordinate with iron ions. The color development results are shown in Figure 5. The intersection coordinates are $x = 0.09$, $y = 0.47$, that is the mass ratio of ferric chloride to sodium lignosulfonate is 0.09, and the mass ratio of sodium lignosulfonate to ferric chloride is 10.8, which shows that 1 g of ferric trichloride can effectively coordinate with 10.8 g of sodium lignosulfonate.

Fig. 5 Relationship between mass ratio and absorbance of ferric chloride and sodium lignosulfonate

Industrial alkali lignin and iron ions are used for color development, as shown in Figure 6. The coordinates of the intersection point are $x=0.06$, $y=0.52$, that is, the mass ratio of ferric chloride to alkali lignin is 0.06, and the mass ratio of alkali lignin to ferric chloride is 15.8, then 1 g of ferric chloride can be compared with 15.8 g of alkali lignin is effectively coordinated.

Fig. 6 Relationship between mass ratio and absorbance of ferric chloride and alkali lignin

4 Conclusion

On the one hand, through the study of the coordination ratio of monophenols, bisphenols and triphenols to ferric chloride, it is found that the effective coordination numbers of these three phenolic compounds are close to the theoretical value, but they are less than the theoretical value, on the other hand, the method can be used to quantitatively analyze the coordination ability of industrial tannic acid, sodium lignosulfonate and alkali lignin with iron ions, which provides a simple and reliable method for the quality analysis of industrial polyphenols.

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