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Improvement on Determination Method Esterification-Rate During Chloroacetate Esters Production Process†

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The result of esterification reaction, as the middle control, plays a key role in production of chloroacetate esters. Usually the esterification of sample was calculated by its acid values and the sample is titrated by the standard solution of potassium hydroxide ethanol before and after the reaction. We proposed to use the standard solution of sodium methoxide ethanol to substitute for the conventional potassium hydroxide ethanol standard solution. By analyzing the ester rate of isopropyl chloroacetate and isooctyl chloroacetate reaction solutions, we found the ester hydrolysis effectively suppressed in our new method. Chromogenic time was changed from original 5-8s to 1-2.3 min, thus the endpoints could be more easily identified. By the test of verification of the mixture of chloroacetic acid and chloroacetate esters, test results were more accurate in analysis.

Key Words: Chloroacetate ester, Esterification rate, Sodium methoxide ethanol, Acidity.

INTRODUCTION

Chloroacetate esters are important organic chemicals, which are extensively used in the fields of organic synthesis, pharmacy, pesticide *etc*. Rare instruments can be used during the reaction to identify the end point of esterification of chloroacetic acid since the chloroacetic acid is a corrosive acid. Chemical analysis is a relative simple, convenient operation and not vulnerable influenced by other factors, which defines the esterification rate as the reaction endpoint and thus can be widely adopted by manufacturers[1-3].

Conventional chemical analysis method is based on the international standards ISO 1385-4-1977[4], (while in China, we usually adopt the acidity and ester quantity analysis method of national standards GB/T1668-2008[5]), which is the esterification rate determination method. The acidity of samples was titrated by potassium hydroxide ethanol standard solution before and after reaction and after a series of calculations we can then get the esterification rate[1-5] of the sample. It is widely known that chloroacetic ester is easy to hydrolyze when water exists. Because of chloroacetic ester inclines to hydrolyze with water especially with alkaline solution. The biggest problem encountered in conventional reaction analysis result arises from the fact that the neglect of the chloroacetic ester hydrolyzation. The hydrolyzation which occurs between chloroacetic ester and the water from titration solution or the reaction of alkali (potassium hydroxide, sodium hydroxide) reacts with acid.

We proposed some improvements on the present chemical analysis of esterification rate-titration method, namely, acidity titrate method. In this paper, standard solution of potassium hydroxide ethanol was replaced by sodium methoxide ethanol standard solution in analysis method. There was no ester hydrolysis found after using sodium methoxide ethanol solution during samples analysis. The colour of solution remained for a long time after the titration endpoint. Hence, the endpoints were more easily identified and test results were more accurate in analysis.

EXPERIMENTAL

Potassium hydroxide: [KOH] = 0.02 mol/L, [KOH] = 0.05 mol/L, 95 % alcohol standard titration solution were prepared and standardized according to GB/T 603.

Sodium hydroxide: [NaOH] = 0.05 mol/L, [NaOH] = 0.1 mol/L standard titration solution were prepared and standardized according to GB/T 601.

Phenolphthalein indicator solution: 10 g/L, which was prepared according to GB/T 603.

Bromocresol purple indicator solution: 1 g/L.

Sodium methoxide standard solution: Firstly, adding certain amount of sodium methoxide (or sodium methoxide

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solution) into a volumetric flask, then, diluted it with ethanol to 250 mL. Finally, hydrochloric acid was used to calibrate concentration of the standard solution which according to the standard HG-T2561-1994 sodium methoxide methanol solution calibration method, then we got the [CH_3ONa].

Isopropyl chloroacetate and isooctyl chloroacetate are obtained by catalyzed esterification reaction, which containing isopropyl chloroacetic acid, chloroacetic acid, isopropyl alcohol or isooctyl chloroacetate or isooctyl alcohol.

Isopropyl chloroacetate and chloroacetic acid mixture solution were prepared by isopropyl chloroacetate, isopropyl alcohol and chloroacetic acid in proper proportion. Isooctyl chloroacetate and chloroacetic acid mixture solution were prepared by isooctyl chloroacetate, isooctyl alcohol and chloroacetic acid in proper proportion.

Determination method and analysis steps: 0.25 mL phenolphthalein indicator solution or 1 mL bromocresol purple indicator solution was added to 50 mL anhydrous ethanol and 0.1 mol/L sodium hydroxide or 0.02 mol/L (0.05 mol/L) potassium hydroxide ethanol solution was used to neutralization until the solution changed to weak pink or green.

3 g Samples was weighted in erlenmeyer flask (accuracy to 0.0001 g), then neutralized solution was added to it until the samples completely dissolved. 0.1 mol/L sodium hydroxide standard solution or 0.02 mol/L (0.05 mol/L) potassium hydroxide ethanol standard solution was used during titration and the titration time completed controlled within 30s. The solution colour turned to weak pink (or green) and kept not fade for 5s, which is the endpoint.

Analyses of the reaction products were performed by means of National Standards of People's Republic of China GB1668-2008 and International Standards of ISO 1385-4-1997. The calculated equation of acid value X is $X = M \times 10^{-3} \times V \times C/m$; the unit of M is g/moL; the V is volume of potassium hydroxide (unit is mL); the G is mass of ester. The C is concentration of potassium hydroxide (unit is mol/L). The calculated equation of esterification rate Y is $Y = (1- B/A) \times 100$ %. The A is acid value before the reaction. The B is acid value after the reaction.

Improved method: Potassium hydroxide ethanol or sodium hydroxide standard solution was substituted by sodium methoxide ethanol standard solution in above analysis method.

RESULTS AND DISCUSSION

The acidity of chloroacetic esters samples were titrated by potassium hydroxide ethanol standard solution before and after reaction in convention analysis method. The hydrolyzation of the chloroacetic ester emerged in the titration process.

Since the potassium hydroxide 95 % alcohol standard solution and sodium hydroxide standard solution were used during the analysis progress, the test result was susceptible because samples were easy to hydrolyze with the water, which came from standard solution or generated by reaction during titration process,

Analysis principle: sodium hydroxide (potassium hydroxide) was used to neutralize unreacted chloroacetic acid and alcohol during esterification. Phenolphthalein was used as indicator. We can calculate the acidity after the titration:

$$\text{R-COOH} + \text{NaOH} \longrightarrow \text{R-COONa} + H_2O$$

The water generated from this reaction and titration standard solution can lead to reversible esterification reaction-hydrolysis reaction (saponification) occurring:

$$\text{R-COO-R'} + H_2O \rightleftharpoons \text{R-COOH} + \text{R'-OH}$$

Esters hydrolyzation speed up as time increasing, acid and alcohols were generated after reaction. Hydrolyzation rate is related with the nature of the ester itself. Alkaline conditions can accelerate ester hydrolyzation rate. The water caused interference on titration endpoint, especially, the influence of the water generated during the titration process was obviously. As a result of the above reasons, the pink colour of solution disappeared soon in less than 5s after the emergence of endpoint. After several times, we only can scrape to over 5s. From Table-1 it is observed that the fade time of solution was only equal to or slightly greater than 5s. Low esterification rate productions were influenced obviously.

TABLE-1
ANALYSIS OF CHLOROACETIC ESTERS SAMPLES BY USING STANDARD SOLUTION OF POTASSIUM HYDROXIDE ETHANOL

Sample	Standard solution of potassium hydroxide ethanol			
	Acid value*	Sample quality (g)	Esterification rate (%)	Fade time(s)
Isopropyl chloroacetate[1]	5.7	2.9262	67.95	5
Isopropyl chloroacetate[2]	3.55	3.0160	80.63	7
IiIsopropyl chloroacetate[3]	3.02	2.9901	83.38	8
Isooctyl chloroacetate[4]	3.57	3.0645	73.57	5
Isooctyl chloroacetate[5]	0.80	2.9787	93.50	8
Isooctyl chloroacetate[6]	0.31	2.9041	97.45	8

Mark: Table 1,2,4,5 are reaction solution, 3,6 are mixture of chloroacetate esters and chloroacetic acid; *Acid value: alkali mg/g product

The original standard was used in plasticizer esters analysis. Titration can be completely finished during standard specified titration time due to slow hydrolyzation rate and analysis error was also small. However, chloroacetic esters hydrolyzation rate was fast, in the role of water in aqueous solution and generated from reaction, hydrolyzation rate became fast, it was difficult to finish titration within stipulated 30s and the colour of neutralization reaction solution endpoint can not maintain 5s or more.

No water generated during titration process with sodium methylate alcohol standard solution: As follow reaction equation:

$$\text{R-COOH} + NaOCH_3 \rightleftharpoons \text{R-COONa} + CH_3OH$$

We can see no water generated after reaction. The hydrolysis of chloracetate can be avoided without water which can be verified from Table-2. Pink (or green) colour disappeared after maintaining for 1 min, whereas the pink colour was easily disappeared by using potassium hydroxide 95 % ethanol standard solution in conventional method. The endpoint was extremely obvious in improvement method.

TABLE-2
ANALYSIS OF CHLOROACETIC ESTER SAMPLES BY USING STANDARD OF SOLUTION SODIUM METHOXIDE

Sample	Standard solution of sodium methoxide ethanol			
	V CH_3ONa (mL)	Sample quality (g)	Esterification rate (%)	Fade time (min)
Isopropyl chloroacetate[1]	3.98	2.3233	70.18	1
Isopropyl chloroacetate[2]	2.90	2.9407	82.84	1.5
Isopropyl chloroacetate[3]	2.78	2.9929	83.83	2
Isooctyl chloroacetate[4]	2.61	2.8789	76.15	1.7
Isooctyl chloroacetate[5]	0.69	2.9170	93.78	2
Isooctyl chloroacetate[6]	0.20	2.9305	98.23	2.3

Mark: Table 1,2,4,5 are reaction solution, 3,6 are mixture of chloroacetate esters and chloroacetic acid

The samples used were prepared by same method (Tables 1 and 2). The quantity of chloroacetic acid of sample 3 was the ratio of proportioning sample mole: ratio of initial reaction solution mole = 0.1623:1; the quantity of chloroacetic acid of sample 6 was the ratio of proportioning sample mole: ration of initial reaction solution mole = 0.0172:1. The ratio of initial reaction solution component mole is according to the chloroacetate ester data from Xue *et al.*[2,6].

Comparing Tables 1 to 2, we found that the ester rate of sample 3 and sample 6 were identical with the actual proportion after using sodium methoxide ethanol standard solution during titration and analysis. However, the original method was influenced by hydrolysis reaction and thus caused deviation. The samples of low ester rate were influenced obviously. The difference of sample 1 in Tables 1 and 2 reached 2.23 %.

The lower ester rate is, the larger deviation after using original method is. The reason scan be analyzed probable is that the samples with lower ester rate, larger amount of unreacted alcohol forms azeotrope with water. Hence, hydrolysis reaction has a great effect on the results during titration process.

Analysis results of different varieties esters is inconsistent: In this paper, isopropyl chloroacetate and isooctyl chloroacetate were adopted for analysis. We found that ester hydrolysis rate is inconsistent for different varieties of ester, which is shown in Table-1and Table-2. This is because the steric effect of ester[7]. Xu Yun *etc.*[6] studied a series of chloroacetate esters rate. From the data we can see that steric hindrance effect ester rate. Different ester has different R' group, the larger its steric hindrance is, the smaller its ester rate and hydrolyzation rate are. Different steric configuration of chloroacetate esters lead to different hydrolyzation rate with the existence of alkali and water, which is verified in this paper.

Conclusion

According to the acid-base theory, standard solutions of different alkalies can be used to determine the esterification rate. Sodium hydroxide in 95 % ethanol was used as titration solution influenced the experimental result, because the water of solution and the water generated during titration process were easily to make hydrolyzing products. Esters hydrolyzation rate is accelerated due to the presence of alkali. The low the products with esterification rate were influenced obviously.

Different species of chloracetate ester has different hydrolysis rate, so the water from the standard solution of alkali or generated during the titration process can affect the results of analysis in the different extents.

After using alcoholic solution of sodium methoxide, without absence of generated water, titration endpoint can remain colour unchanged. During test and verify process, the endpoint was easy to judge. The improvement method avoided ester hydrolysis, which made test results more accurate.

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