Simple and Quick Quality Confirmation Method of Aqueous Urea Solution for Marine SCR System

Evaluation of Alkalinity of Aqueous Urea Solution with LAQUAtwin pH Meter

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The quality requirements of aqueous urea solution at 40% concentration for Marine Selective Catalytic Reduction (SCR) system is defined by International Standard (ISO-18611). One of them is the alkalinity which determined by potentiometric titration of free ammonia in the urea solution with hydrochloric acid solution. However, the titration is time-consuming work, and there are no crew being familiar with the chemical experiment, and no operation place in the ship. This paper shows compact water quality meter LAQUAtwin pH can be used for the simple and quick evaluation of aqueous urea solution quality.

Introduction

The International Maritime Organization (IMO) NOx Tier III standards are applied to all ships constructed after 1st January 2016 having marine diesel engine with an output power of 130 kW or more. These new standards require the emission of NOx from ships to be reduced by 80% compared to restriction from Tier I (2000). The need for systems able to reduce NOx emissions is therefore recently increasing.

One of the methods for the reduction of NOx emissions is called the Selective Catalytic Reduction (SCR). In a SCR-based system, an aqueous urea solution is used to generate ammonia by hydrolysis.

$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3 \cdots\cdots (1)$$

The generated ammonia will ultimately reduce NOx species in a reaction that generate nitrogen and water, that can be harmlessly discharged to outside.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \cdots\cdots (2)$$
$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \cdots\cdots (3)$$

Thus, the quality of the aqueous urea solution is a crucial factor for the reduction of NOx emissions.

A standard aqueous urea solution (40%) used in the SCR of ship engines must satisfy 14 criteria from the International Standard ISO18611.[1] One of these criteria is that the alkalinity of the solution, which is determined as the percentage of ammonia, should not exceed 0.5%.[1][2] The standard method to determine the alkalinity of an aqueous urea solution is a neutralization titration using hydrochloric acid.

The hydrolysis reaction of the aqueous urea solution will occur even at room temperature and will ultimately deteriorate performances of the SCR as the alkalinity of the solution is increasing, ammonia being generated.[3] In a ship, a high quality maintenance is very challenging as the aqueous urea solution is stored onboard where high temperature conditions are common.

Onboard monitoring for the alkalinity of the aqueous urea solution is therefore essential. The neutralization titration method defined in ISO is nevertheless a complicated procedure to be implemented for a ship crew who is lacking knowledge and experience of chemicals. In addition, it is difficult to use the urea solution for SCR during voyage if they request to inspection facility. In this paper, we introduce a quick and simple method to certify onboard the quality of an aqueous urea solution.

Alkalinity of aqueous urea solutions

Procedures

The determination of the alkalinity of an aqueous urea solution was done according to the standard ISO18611-2 (Appendix D). 1 mL of 40% aqueous urea solution (density = 1.11 g/mL[1]) was added in a beaker containing 100 mL of pure water. The obtained solution was then titrated with a solution of 0.01 mol/L HCl until a pH of 4.5 could be measured using a calibrated pH electrode.[2]

The formation of NH_4Cl is done from NH_3 and HCl with an equimolar ratio (Equation 4). The alkalinity of the aqueous urea solution can therefore be deduced from the volume of 0.01 mol / L HCl used for the titration

(Equations 5, 6).

$$NH_{3\text{ in urea soln.}} + HCl \rightarrow NH_4Cl \quad \cdots\cdots (4)$$

$$\text{Alkalinity (\%)} = \frac{\text{The ammonia mass (g)}}{\text{The test potion mass of urea solution (g)}} \times 100 \quad \cdots\cdots (5)$$

$$\text{Alkalinity (\%)} = (0.017\ V)\ /\ m_s \quad \cdots\cdots (6)$$

V : The volume of the hydrochloric acid solution (0.01 mol/L) used for the titration (ml)

m_s : The mass of the test portion of urea solution (g).

Simple determination method for deterioration of the aqueous urea solution

Principle

By definition, 1 mL (1.11 g) of a 40% aqueous urea solution with an alkalinity of 0.5% requires adding 30 mL of 0.01M HCl to reach a pH of 4.5. As shown in the model for the titration curve (Figure 1), a fresh urea solution (alkalinity < 0.5%) will have a pH lower than 4.5 by the addition of 30 ml of 0.01 M HCl. On the other hand, a deteriorated urea solution (alkalinity > 0.5%) will have a pH higher than 4.5 by the addition of 30 ml of 0.01 M HCl. A measurement of the pH from a mixed solution of 1 mL of 40% urea solution and 30 mL of 0.01 M HCl can therefore judge the deterioration of an aqueous urea solution.

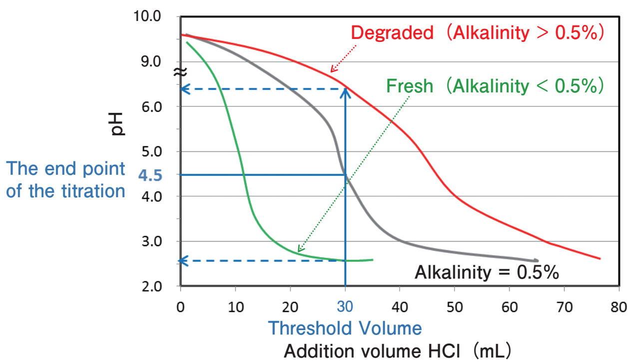


Figure 1 Model for the titration curve of 40% urea solution with 0.01 mol/L HCl

Aqueous urea solution test kit

Kit for an aqueous urea solution test have been developed to be available on site following the principle of the simple method described above. An issue with inboard is variation of the temperature. At high temperature, the high volatility of the hydrochloric acid will decrease the concentration of HCl in the solution, which yield to a loss of accuracy for alkalinity measurement. Sulfuric acid, on the other hand, is a strong acid having no volatility and was therefore selected as an alternative for HCl. Figure 2 shows titrations using both hydrochloric acid and sulfuric acid, for fresh and degraded aqueous urea solutions. Sulfuric acid gives 2 protons per molecule and, compared to HCl, the molarity of sulfuric acid required for the titration is half. The results from the neutralization titration was the same for both type of acid. Sulfuric acid could therefore be adopted for tests.

The kit contains a 15 mL bottle of 0.01 mol / L (0.02 N) sulfuric acid (single use), a 1 mL syringe for measurement and a compact LAQUAtwin pH meter. All parts are embedded in a carrying case (Figure 3a). The LAQUAtwin pH meter combines an integrated sensing unit and a portable display. This lightweight meter can be carried with one hand and does not require a beaker, important requirement for field measurements. The operation method is as followed. At first, 1 mL of 40% urea aqueous solution is withdrawn with a syringe and is put into a bottle containing sulfuric acid. The mix is closed

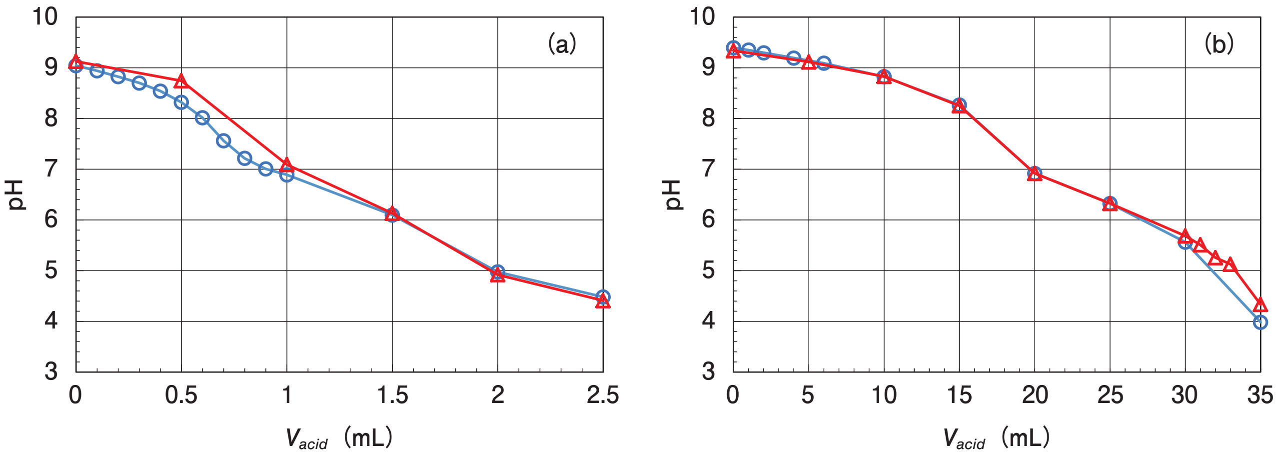
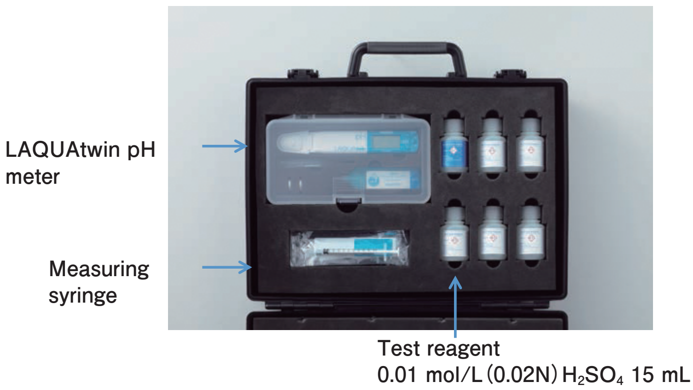
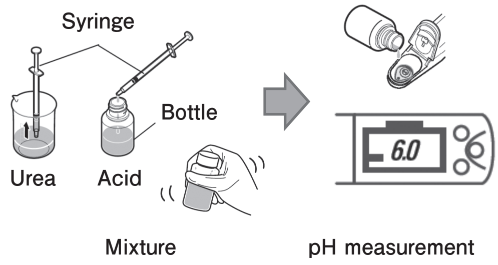


Figure 2 Comparison of neutralizing efficacy of HCl and H_2SO_4 in aqueous urea solution.
(a) Neutralizing titration in fresh urea solution; (b) Neutralizing titration in degraded urea solution.
0.01 mol/L hydrochloric acid (○); 0.005 mol/L sulfuric acid (△)
The degraded urea solution was which the fresh urea solution was stored under 60℃ for 2 weeks.



(a) Contents



Result	Judgement	
Under pH4.5	Good	ISO-18611-2 Alkalinity < 0.5%
pH4.5 or above	Poor	ISO-18611-2 Alkalinity ≧ 0.5%

(b) Simple and quick operation

Figure 3 Aqueous urea solution test kit

with a lid and stirred to ensure the homogeneity. And then the mixture is set in the sensing section of the calibrated LAQUAtwin pH meter (Figure 3b). The quality of aqueous urea solution can finally be judged by reading the pH of the mixture. As described above, pH measurement using LAQUAtwin pH meter makes possible an easy and quick determination for the deterioration of an aqueous urea solution.

Results and Discussion

The good correlation of alkalinity values obtained by our simple determination method and by the neutralization titration method of the international standard ISO confirms the effectiveness of the test kit. Figure 4 shows pH measurements performed with the kit and the alkalinity determined by neutralization titrations, using an aqueous urea solution in which the deterioration has been accelerated by heating at 60°C. The two points (○, ●) from different sample preparations confirm the reproducibility of our method. The threshold for the deterioration of the solution[4] was set to be pH = 4.5 / 0.46% (≈ 0.5%) of the alkalinity. There were no deterioration in the region less than these thresholds values for both methods. A correlation between the 2 methods was also obtained in the deterioration region beyond the threshold value.

The plot point X shown in Figure 4, however, indicated an inconsistency in the deterioration judgement. As the reason for this, the amount of ammonia gas dissolved in

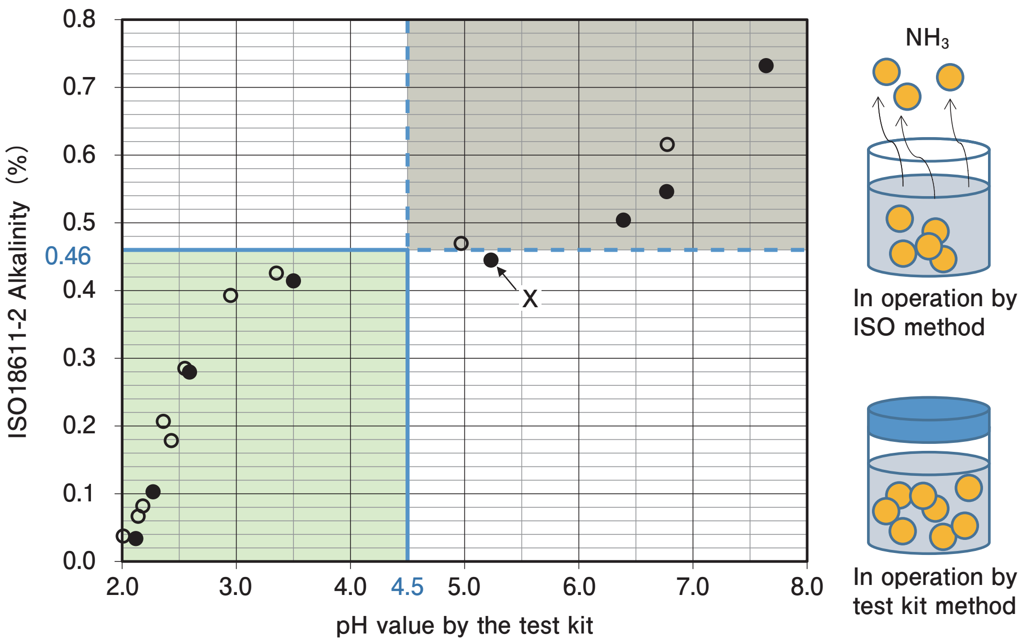


Figure 4 Correlation between ISO method and test kit method
The two symbols (●) and (○) show their individual series of the first and second time examinations.
The alkalinity 0.46% is regarded as 0.5% by rounding a number[4].
The "X" represents the disagreement between the data of two methods.

the aqueous urea solution decreases by a diffusion process into the atmosphere during the neutralization titration operation, which is lowering the alkalinity. Even ISO standards recommend operating quickly because a diffusion of the ammonia gas can alter the accuracy of the measurement[2]. A kit for aqueous urea solution test capable of a quick measurement of the pH value will reduce the interference from the diffusion of the ammonia gas and provides a judgment suitable for the state of the aqueous urea solution.

Conclusion

A quick and simple method for the judgement of the deterioration in an aqueous urea solution using the neutralization titration method was introduced. The result of the judgment by the kit based on this quick and simple method had a good correlation with the alkalinity determined by the method from ISO. Our experiments shows the effectiveness of the LAQUAtwin pH meter to screen the deterioration of an aqueous urea solution.

* This content is based on our investigation at this publish unless otherwise stated.

References

[1] ISO 18611-1:2014, Ships and marine technology - Marine NOx reduction agent AUS 40 - Part 1: Quality requirements

[2] ISO 18611-2:2014, Ships and marine technology -Marine NOx reduction agent AUS 40 -Part 2: Test methods

[3] ISO 18611-3:2014, Ships and marine technology -Marine NOx reduction agent AUS 40 -Part 3: Handling, transportation and storage

[4] JIS Z8401:1999, Guide to the rounding of numbers

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