

## Acoustical Method for Stoichiometric Point Detection of Neutralization Titration

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### Abstract

In this paper, we attend to changes of temperature caused by heat of neutralization and detect a stoichiometric point from measurements of the propagation velocity of sound in a liquid solution. The transducers, i.e. the transmitter and receiver consist of piezoelectric ceramic plate size of 5(L) × 5(W) × 0.65(D) mm<sup>3</sup>. The changes of sound velocity can be observed by the phase difference. Neutralization of 200 ml of 1 mol/l NaOH(aq) with 2 mol/l HCl(aq) and 200 ml of 1 mol/l NH<sub>3</sub>(aq) with 2 mol/l CH<sub>3</sub>COOH(aq) were measured under the condition of the frequency of 3.618 MHz and the propagation distance of 11 mm. Both of the experimental results in phase differences show gradient changes at the stoichiometric point of neutralization. As the results also include the changes of concentration, the stoichiometric point can be detected from the change of the phase difference between two transducers.

**keywords:** ultrasonic, acoustic wave, temperature measurement, neutralization, end point

### Introduction

Recently, many industrial processes are automated even in wastewater treatments or their quality inspections. As “pH”, hydrogen ion concentration, is one of the well-known reference index to inspect a condition of substances[1], the control of the pH neutralization process performs an important role in many places, such as chemical industries[2], food industries[3], etc. The electric method with glass electrodes and the colorimetric method by indicators are widely used in pH measurement, and other methods have been studied[4-6]. The colorimetric methods potentially contain a personal equation and an error. Since the electric method using a pH meter can measure precisely, it is built into automatic pH control systems[7]. The weak point of the glass electrode is that it is necessary to keep the surface of the electrode clean for precise observations[2]. As the glass electrode is installed in solutions directly, it needs regular cleaning.

Acoustic techniques make it possible to measure in non-contact and real-time. As acoustic waves can transmit various states of matter, such as vapor[8], liquid[9,10] and solid[11], acoustic measurement is used for thermometry[8], acoustic computerized tomography (A-CT)[12], densitometer[13], etc. Since sound velocity which propagates in a liquid solution depends on a concentration and temperature of the

solution[13], measurements of one of the two conditions, with the other fixed, have been studied[13,15-17].

In this paper, we present a new method of detecting neutralization by the measurement of the propagation velocity of acoustic waves. The temperature of the solution changes by the neutralization heat. Consequently the sound velocity propagated through the solution also changes depending on the temperature. The transducers usage in the solution indicates the change of the temperature as the change of the phase difference between two transducers. The acoustic method of detecting neutralization has advantages of nondestructive, non-contact and sustainable measurement.

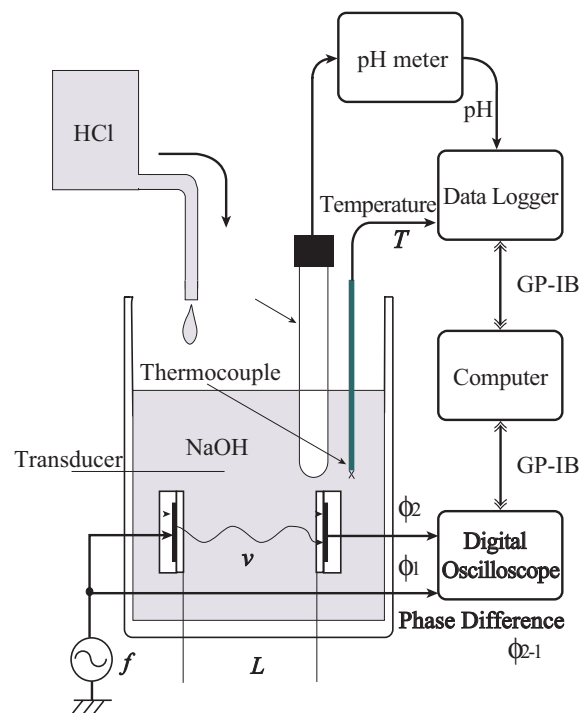


Figure 1: Schematic diagram of a “neutralization equivalent detector.” Temperature changes of a solution are translated into the phase difference between the input and output signals. Dropping speed is uniformly held by a dropper. Phase difference is measured by an oscilloscope. Thermocouple and glass electrode are also installed into the solution, and digitized by a data logger. All data are recorded on a PC via the general purpose interface bus (GP-IB).

**Principal**

*Brief overview of detection*

In the customary way, the glass electrode detects the change of hydrogen ion concentration caused by neutralization. Neutralization also changes the temperature of the solution by its reaction heat. It can be measured by thermocouple. However thermocouple measured only the point of the temperature of contacting region where it is installed. On the other hand, temperature of the solution controls the sound velocity propagated through the solution. The changes of sound velocity can be observed by the phase difference therefore the end point of neutralization is detected.

*Temperature measurement of solution*

A schematic diagram of a monitoring appliance of the neutralization titration is shown in Figure 1. A pair of ultrasonic transducer, consisted of piezoelectric ceramic plates, is arranged in a solution with distance  $L$  between the pair, i.e. the transmitter and the receiver. Ultrasound with frequency  $f$  which is radiated from the transmitter propagates through the solution with velocity  $v$ , and received by the opposite receiver. As sound velocity depends on the temperature of the medium, alterations in sound velocity show changes of the temperature in the medium. Phase difference  $\phi_{2-1}$  is defined as

$$\phi_{2-1} = \phi_2 - \phi_1, \quad (1)$$

where  $\phi_1$  and  $\phi_2$  are phases of input and output signals, respectively. Though the phase difference is the sum of acoustical phase delay  $\phi_A$  and electrical phase delay  $\phi_E$ , phase difference  $\phi_{2-1}$  in this experiment means the former delay because the latter delay is almost fixed zero. The acoustical phase delay is expressed by the function of the mean temperature of the propagated area as

$$\phi_{2-1} = \phi_A = -\frac{2\pi f L}{v}. \quad (2)$$

Therefore, the phase difference  $\phi_{2-1}$  shows the difference of the sound velocity.

*Neutralization reaction*

We shall suppose that a volume of  $n$  of strong base NaOH of molar concentration  $a$  in a beaker are titrated with a solution of a strong acid HCl of molar concentration  $b$ . At the moment of titrating HCl with volume of  $x$  into NaOH solution, hydrogen ion concentration in the beaker can be estimated by the budget of instillation as

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{K_w(an - bx)}{n + x} \quad x < \frac{an}{b}, \quad (3)$$

$$[H^+] = \frac{an - bx}{n + x} \quad x > \frac{an}{b}, \quad (4)$$

where  $K_w$  is an ion product for water which can be

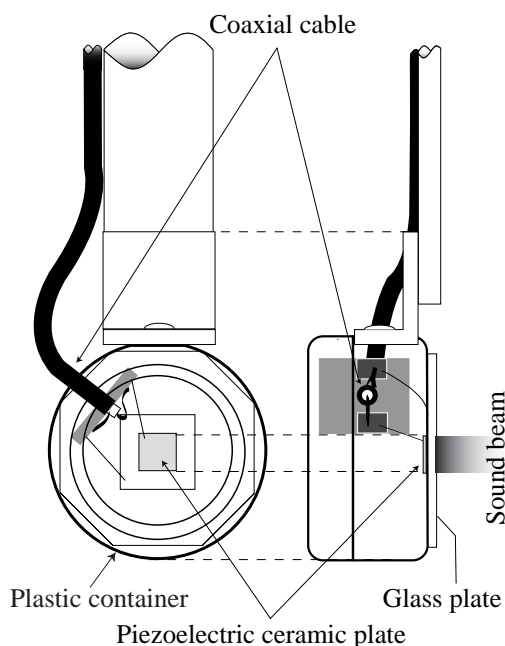


Figure 2: Schematic front and side view of transducer. Piezoelectric ceramic plate bonded on to a glass plate and covered in a plastic container to protect from pervasion of solutions.

interpreted about  $10^{-14}$ . It then follows, by the negative logarithms of both sides, that

$$pH = 14 - \log(an - bx) + \log(n + x) \quad x < \frac{an}{b}, \quad (5)$$

$$pH = \log(n + x) - \log(bx - an) \quad x > \frac{an}{b}. \quad (6)$$

As the heat released from neutralization is known as a value of 56.48 kJ/mol, thermochemical equation of NaOH and HCl is written by



In this case, we suggest that all heat of neutralization is used as the rise of temperature of solution and there will be no disclosure of heat. In addition, reaction coincides with dropping, and time delay does not occur in propagation of the heat. Thereupon rise in temperature can be expressed by

$$\Delta T = \frac{Q}{mc(n + x)}, \quad (8)$$

where  $m$  and  $c$  are the specific gravity and the specific heat of the solution, respectively.

**Experimental setup**

The titrations were operative with a medicine dropper to keep a dropping speed at a constant state. The speed was checked by counting the number of drops in a dropping tube for every 15 seconds. The amount of dropping in 15 seconds was measured with a graduated cylinder, and then the capacity per drop and dropping speed were calculated from the results.

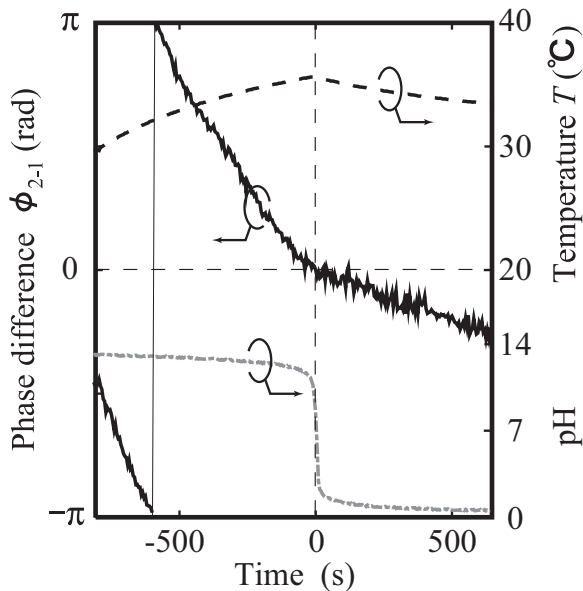


Figure 3: Experimental results under neutralizing NaOH 200 ml by HCl. NaOH and HCl were 1 mol/l and 2 mol/l of concentration, respectively. Temperature and pH of the solution in a beaker, phase delay between input and output waves under distance between transducers about 12mm, input frequency 3.618 MHz. 1st trace: temperature changes of solution measured by thermocouples, 2nd trace: phase difference between input and output signals measured by a digital oscilloscope, 3rd trace: pH of solution measured by glass electrode. “0” point of phase difference and time is indicated on the basis of the end point.

The transducers, i.e. the transmitter and the receiver consist of piezoelectric ceramic plate (102A /TDK) size of  $5 \times 5 \times 0.65 \text{ mm}^3$ . The transmitter and receiver were of the same configuration. The configuration of the transducer is shown in Figure 2. Since the piezoelectric ceramic plate was arranged on a glass plate and covered in a plastic container, it was protected from pervasion of solution.

The transducers were installed into a 1000 ml beaker with a thermocouple and a glass electrode. A magnetic stirrer was used so that reaction heat might be equally transmitted in the solution. In order to avoid observations of triple transit echo (TTE) by the two facing transducers, the direction of one transducer was changed a little. Phase difference  $\phi_{2-1}$  was digitized by an oscilloscope (54657A / Agilent Technology) for four times in every five seconds and the averages were taken. Temperature of the solution  $T$  is measured by a “Teflon” coated thermocouple put near the transducer, and hydrogen ion concentration pH was measured by a glass electrode of a pH meter

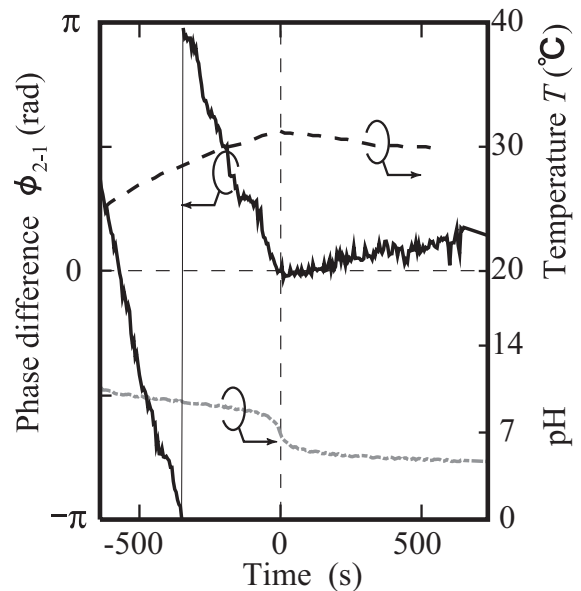


Figure 4: Experimental results under neutralizing NaOH 200 ml by HCl. NaOH and HCl were 1 mol/l and 2 mol/l of concentration, respectively. Temperature and pH of the solution in a beaker, phase delay between input and output waves under distance between transducers about 12mm, input frequency 3.618 MHz. 1st trace: temperature changes of solution measured by thermocouples, 2nd trace: phase difference between input and output signals measured by a digital oscilloscope, 3rd trace: pH of solution measured by glass electrode. “0” point of phase difference and time is indicated on the basis of the end point.

(HM-5S / DKK-TOA) for reference. They were also measured in every 5 seconds, and were automatically read out by a data logger (34970A / Agilent Technology). All data were recorded by PC via the general purpose interface bus (GP-IB) in real-time.

### Experimental Result and Discussion

Experimental results of neutralizing NaOH 200 ml by HCl,  $\text{NH}_3$  200 ml by  $\text{CH}_3\text{COOH}$  are shown in Figure 3 and Figure 4, respectively. The upper trace shows the temperature changes of solution measured by thermocouples, the second trace is the phase difference between input and output signals measured by the digital oscilloscope, and the third trace is the pH of the solution measured by the glass electrode. NaOH and HCl were about 1 mol/l and 2 mol/l of the concentration, respectively. The room temperature of the laboratory was about 31 degree Celsius.  $\text{NH}_3$  and  $\text{CH}_3\text{COOH}$  were also about 1 mol/l and 2 mol/l of the concentration, respectively. The room temperature of the laboratory was about 23 degree Celsius. The

distance between the transducers was 12 mm and frequency was 3.618 MHz. HCl and CH<sub>3</sub>COOH had been dropping after the end point.

"0" point of phase difference and time is indicated on the basis of the end point. The attainment to an end point of neutralization was determined from the value of the pH meter. The elapsed time until the neutralization of NaOH and HCl was 736 seconds, and dropping volume implied from the ending time was 109 ml. Speculative neutralization equivalent derived from the concentrations in this experiment was about 110 ml. The elapsed time until the neutralization of NH<sub>3</sub> and HCl was 810 seconds, and dropping volume implied from the ending time was 109 ml. The temperature of solution was rising by the liberated thermal energy while neutralization progressed. After the end point, heat occurrence terminated, and with this, temperature of solution fell slowly. Clear change of gradient in the trace proves the end point specifically. Phase difference also changed along with the progress of neutralization. The point of the inflection in the phase difference trace occurred. Here we can detect the end point.

After the end point, though temperature fell slowly, phase difference in titration of NaOH and HCl still continued. If phase difference simply depends on the change of temperature in the solution, the trace of phase difference should also rise. On the other hand, the trace of phase difference in titration of NH<sub>3</sub> and CH<sub>3</sub>COOH clearly rose. It is possible to say that concentration change of the solution has much effect on the sound velocity. But this does not affect the detection of neutralization.

### Conclusion

A new method of detecting neutralization by the measurement of the sound velocity propagation velocity of acoustic waves in a liquid solution has been introduced. In the experiment using 3.618 MHz-ultrasonic probe, change of the temperature was found to occur as the change of the phase difference between the input and output signals of the probe. The end point of neutralization NaOH 200 ml by HCl and NH<sub>3</sub> 200 ml by CH<sub>3</sub>COOH could be detected from the change of gradient of phase differences under the following conditions that the distance between two transducers and concentrations of aqueous base and aqueous acids were 12 mm, 1 mol/l and 2 mol/l,

respectively. This is almost the same time that the pH meter displayed pH=7.

In this present experiment, the two transducers were installed directly into the solution. Our future experiment will be designed so as to attach the transducers outside the solution receptacle, facing each other. This system enables pH monitoring at wastewater treatment system with real time responses, nondestructive and non-contacted measurement.

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