# Inadequacy of Water Band Movement Technique for Kinetic Interpretation of RCOOH–NaHCO$_3$ Reaction

P Sahoo and B Saha
Ultra Sensitive Devices and Techniques Section, SHINE Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, Tamil Nadu, India.

The kinetic parameters derived from simple measurements of the movement of water band in a glass tube grossly underestimate the rates of reactions between the chosen carboxylic acids and sodium hydrogen carbonate. Measurements by a conductometric technique indicate that the reported parameters are more in line with the kinetics of carbon dioxide escape from aqueous solutions under the given experimental conditions.

Reason for Review of Water Band Technique

This communication is with reference to an illustrative experiment which has been published in the Classroom section of *Resonance*, Vol. 3, No. 10, pp. 89–95, 1998. This technique is based on the movement of water band in a glass tube to arrive at the kinetic parameters for the reaction between RCOOH and NaHCO$_3$. The inference from the measurements was that the rate determining step for the first order kinetics is governed by the dissociation of the carboxylic acid:

$$RCOOH + H_2O = RCOO^- + H_3O^+$$
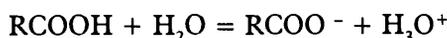
which is the first of the four steps described in the article.

In this technique, the positive pressure needed for pushing the water band is caused by the release of the reaction product, $CO_2(g)$. There seems to be an implicit assumption that the release of CO_2 is much faster than the dissociation of the carboxylic acid. This assumption needs to be validated before conclusions can be drawn with respect to the kinetics of RCOOH–NaHCO$_3$ reactions.

In the reported experiments, positive pressure is manifested in the gas phase only when CO_2 molecules escape the liquid phase. Besides evaporation from the surface, processes such as nucleation, growth and migration of gas bubbles to the gas-

liquid interface occur within the liquid phase prior to escape. These are sufficient reasons for slowing down the release step. In view of these factors, we attempted monitoring the kinetics of $CH_3COOH–NaHCO_3$ reaction by a different technique that can follow the progress of the reaction irrespective of the kinetics of CO_2 release from a solution phase.

Time Dependent Conductance Measurement

There is a net decrease in ionic conductance of solution for the overall reaction between weakly dissociated acetic acid and strong electrolyte $NaHCO_3$:

$$CH_3COOH(aq) + NaHCO_3(aq) =$$
$$CH_3COONa(aq) + H_2CO_3(aq)$$
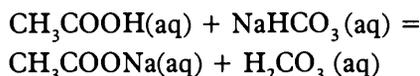
giving rise to ionically conducting sodium acetate and another weak acid, namely carbonic acid. Carbon dioxide evolves as a result of dissociation of carbonic acid as its level in solution exceeds the equilibrium value dictated by the partial pressure of $CO_2(g)$ in the gas phase. The decrease in conductivity is largely due to the difference in the ionic conductances of bicarbonate and acetate anions.

Therefore, if one follows the change in the solution conductance as a function of time from the point of bringing together the two reactants ($NaHCO_3$ and acetic acid solutions), the rate can be determined provided the mixing time for solution homogenisation is insignificant compared to the half time of the reaction.

In our laboratory we have created facilities for time dependent monitoring of solution conductances in static or flowing systems. Measurements can be made at sub-second intervals. We used these facilities for monitoring the kinetics of $CH_3COOH–NaHCO_3$ reaction in dilute solutions. Experiments were planned in such a manner that, for a given set of conditions of stirring, the solution mixing time could also be determined simultaneously. A typical procedure follows.

The target reactant concentrations of ~0.006 M each of CH_3COOH and $NaHCO_3$ were to be realised by the addition of 0.6 ml each of ~1 M of respective stock solutions into 100 ml of demineralized (DM) water within which a vertical conductivity probe was immersed. Data acquisition commenced prior to the addition of reactants (with water alone). Data were sampled at intervals of 0.6 seconds. Region I in *Figure* 1 gives the background data points for water. Sodium bicarbonate stock solution (0.6 ml) was added in two steps. A larger fraction was added in the first step yielding a sharp rise in specific conductance as indicated by the data points in region II. After some time the remaining portion was added (region III). Subsequently, 0.6 ml of ~1 M solution of the other reactant (CH_3COOH) was added to initiate the chemical reaction (region IV). The conductance decreased at a much faster rate than what one would expect from the results published earlier. Data acquisition terminated after recording sufficient points in the flat portion on completion of the reaction.

The time widths during transition from one homogeneous state to the other, corresponding to the first two jumps in the specific conductance versus time data in *Figure* 1 are associated with mixing alone as these were merely due to increase in $NaHCO_3$ concentration. Whereas, the time width during the fall in conductance soon after addition of acetic acid is due to the composite effect of mixing and chemical reaction. The magnetic stirrer settings were not changed during the measurement.
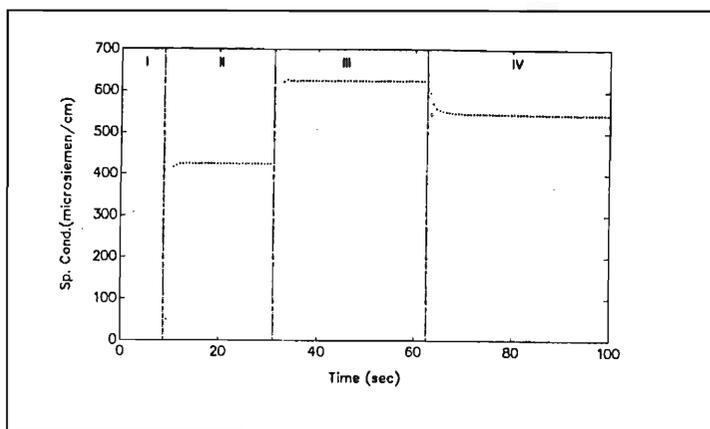
Figure 1. Measured specific conductance data points as a function of time: Region I for 100 ml DM water; region II after addition of first portion (0.4 ml) of ~1 (M) $NaHCO_3$ solution; region III after addition of second lot (0.2 ml) of $NaHCO_3$: region IV after addition of 0.6 ml of ~1 (M) acetic acid solution.

Figure 2. An enlarged view of the time dependent change of specific conductance before and after addition of NaHCO₃ (2nd lot) and acetic acid, respectively. Plots are normalised to instants of addition.
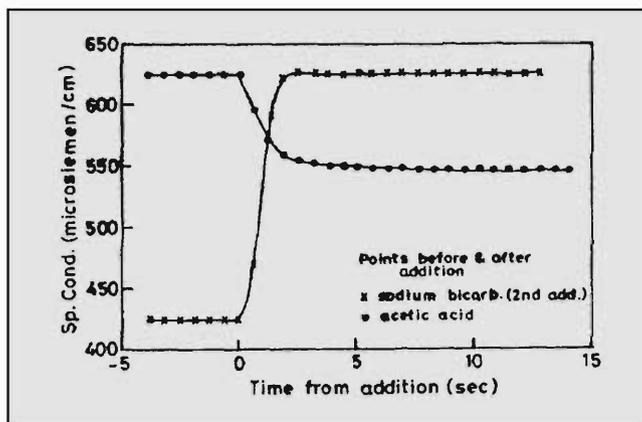
An enlarged version of the plots, normalised with respect to the times corresponding to solution additions, covering regions III and IV are given in *Figure* 2 to assess closely the time dependent positive and negative changes within comparable magnitudes of specific conductances. Half times for conductance change, the time needed for conductance to change from the initial value to the mid value between the initial and final states, can be derived from the stable values before and after addition in these two cases. For both the additions, the half times are almost identical and each is very close to one second. Thus it can be inferred that the reaction between acetic acid and sodium bicarbonate must be proceeding with a half time less than or at best close to one second. Mixing time is the limiting factor for studying the kinetics of such reactions. The decrease in the conductivity after acetic acid addition is indicative of chemical reaction, and that the reaction is complete within the span of measurement is evident from the time invariant stable readings.

The first derivative plot, depicting the rate of change in conductance as a function of time, is given in *Figure* 3. The first two positive peaks are due to the changes on account of $NaHCO_3$ additions. The negative peak is due to changes caused by CH_3COOH addition. It may be noted that the peak widths at half maxima are similar during three additions.

We reached similar conclusions by reversing the sequence of
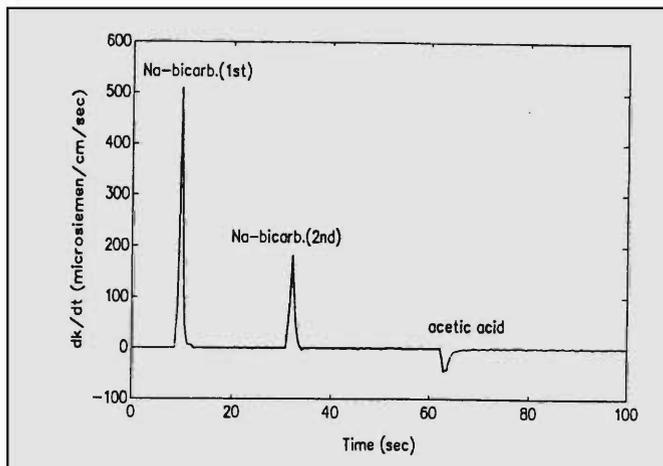
Figure 3. First derivative plot of the data in Figure 1 – the rate of change of specific conductance (k) as a function of time.

reactants addition and by conducting the experiments at higher concentrations. Half times of reaction of sodium bicarbonate with four different carboxylic acids, reported earlier, fell within the range of 20-26 seconds. These times are too long to miss the kinetic effects in measurements by our technique.

On CO_2 Escape Kinetics

What is the possible reason for the gross mismatch between two sets of independent measurements by different techniques? We note strikingly close specific reaction rate constant values, reported earlier, for different acids. It is possible that these data reflect CO_2 escape kinetics rather than the kinetics of the $RCOOH–NaHCO_3$ reactions. With the same volumes of reactants, under similar stirring conditions, one may expect similar rate constants for CO_2 release from solutions.

As an example we present in *Figure 4*, the results of our measurement aimed at determining the CO_2 escape rate from water under air purging. Initially the dissolved carbon dioxide level was enhanced by passing $CO_2(g)$ beyond the normal concentration in water in equilibrium with air. With the onset of air purging through CO_2-rich water, conductance started decreasing exponentially and finally reached the equilibrium value. The linear plot of time versus logarithm of background corrected specific conductance (*Figure 5*) indicate first order
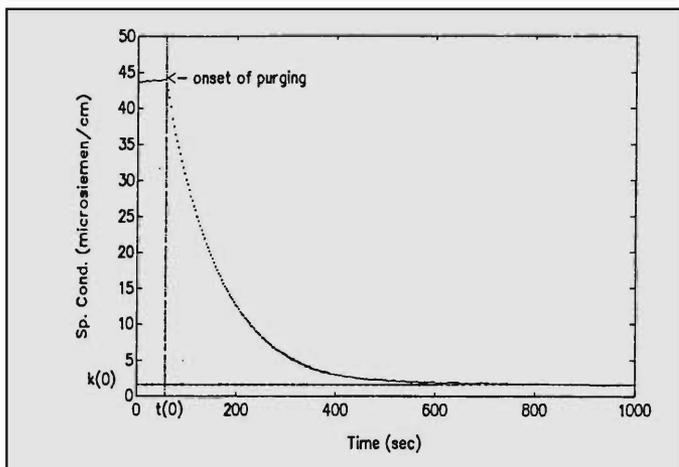
kinetics for CO_2 escape from water. For the given condition of purging, the half time for release was about 72 seconds. It may be noted that the rate of CO_2 release, besides depending on the (dissolved) concentration, also depends on the ratio of the gas-liquid interface area to liquid volume under dynamic condition. Hence for a given concentration, the rate varies depending on the extent of agitation.

In the experiment described in the previous section (*Figures* 2 and 3), attainment of the final state after acetic acid addition was less sharp in comparison with that in the case of $NaHCO_3$ addition. Though the half times (~ 1 sec) are practically the same, slight tailing in the former case is due to slow escape of CO_2 after completion of the acetic acid–sodium bicarbonate reaction.

Figure 5. Linear time dependence of logarithm of background corrected specific conductance, indicative of first order kinetics for CO_2 escape from water.
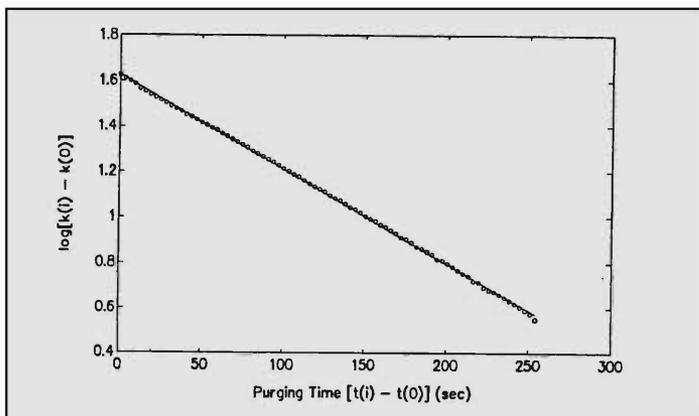
In the experiments published earlier, fixed volumes (10 ml) of reactants in every case in the 150 ml reaction flask might have been subjected to same kind of stirrer-induced agitation to yield half times clustering in the range of 20-26 seconds. We feel that such long half times can not be attributed to the kinetics of carboxylic acid–sodium bicarbonate reactions. Most likely the results published earlier pertain to carbon dioxide escape kinetics under the experimental conditions.

Acknowledgments

Meteors – The Terrestrial and Celestial Connection

B S Shylaja
Jawaharlal Nehru Planetarium,
Bangalore Association for Science Education,
Sri T Chowdaiah Road, High Grounds,
Bangalore 560 001, India.

Introduction

Shooting stars or meteors have fascinated mankind from times immemorial. While it took centuries to realize that they have nothing to do with the stars, the exact physics was understood only in the last couple of centuries. Looking back into the pages of history we note that the study of the phenomenon itself starts with Aristotle's comment that the meteors are atmospheric events. Two hundred years ago, the debate was on their origin – whether celestial or terrestrial?

But we must first know what meteors are. These tiny particles weighing less than a gram float around in the vast space (believed to be almost empty) outside the earth's atmosphere and a chain of complex physical events are created as they enter the atmosphere. They are referred to as meteroids. Depending on the size of the particle, the effects can differ by orders of magnitude. The German duo Heinrich William Brandes and Johann Friedrich Benzenborg were the first to calculate the height at which meteors exist. They did this by the simple

The height at which meteors exist can be calculated by the simple method of triangulation.