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Resolving Complex Chemical Processes: Comparison of Monitoring by Ultrasound with Other Measurement Methods

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Abstract *– A weak acid-strong base time-resolved titration has been monitored by ultrasonic and pH measurements. Various treatments have been applied to the acquired data, and the results obtained are presented and discussed. It has been found that the group velocity of ultrasound is the most robust parameter after enhancement of the time resolution of the ultrasonic hardware by signal processing. Application of temperature correction transformed the ultrasonic titration curves into two nearly straight lines that intersect at the equivalence point of the titration at the maximum point on the curve. The ultrasonic instrument exhibited much lower stabilisation times after titrant addition compared to the conventional pH-meter making ultrasonic spectroscopy potentially very useful for monitoring/controlling fast chemical processes including acid-base reactions.*

Keywords *– ultrasonic process monitoring, ultrasonic signal processing, ultrasonic group velocity, ultrasonic titration curve*

I. INTRODUCTION

Complex chemical processes in aqueous solutions can be resolved by using various analytical instruments, with optical spectroscopy methods being the "most widely used tools for the elucidation of the structure of molecular species as well as the quantitative and qualitative determination of both organic and inorganic compounds" [1]. However these methods can be difficult to apply *in situ*, online, and for opaque media. Some other conventional analytical methods (e.g., electroanalytical techniques) can only provide single point values for a sample solution or they may introduce tough requirements for the sample homogeneity / mixing efficiency. These limitations can be avoided by using ultrasound that can propagate in opaque media and can acquire information about its propagation along the entire pathway.

Propagation of ultrasound in aqueous solution can be considered from the prospective of phase velocity (optionally, versus frequency), attenuation (optionally, versus frequency) and group velocity. As the wavelength of ultrasound is typically in the order of at least tens of microns or more, resonant absorption does not take place normally, and attenuation versus frequency represents smooth curves [2]. The intensity of ultrasound applied to a monitored medium should be small to avoid heating and other alterations to the medium (although ultrasound is used in analytical chemistry for invasive sample preparation as well [3]), and undesirable effects on another analytical instruments [4].

Propagation of ultrasound in electrolytes was studied extensively based on the ionic-atmosphere model developed by Debye and Hückel in 1923 with further refinements. It qualitatively or partially quantitatively described some experimental phenomena related to the dependence of ultrasound velocity on the concentration of electrolyte. This theory was not extended towards non-electrolytes, and its experimental verification was complicated seriously by the low resolution of the previous generation of instruments and strong dependence of ultrasound on temperature that complicated accurate measurements [5].

Various theories based on consideration of relaxation phenomena (thermal [6,7], structural [6,8], chemical [6], shear [8]) led to development of ultrasonic models that qualitatively and quantitatively described ultrasonic absorption in homogeneous media versus frequency at different temperatures. This approach has been extended further for binary mixtures like colloids, emulsions etc [2].

Some phenomenological macroscopic models for determining ultrasonic velocities in binary and ternary mixtures were applied to experimental data in [9], but a partial fit only was achieved.

Overall, although theoretical models for both ultrasonic velocity and attenuation have been elaborated and extensively refined for stationary conditions in a chemical sense, they could be difficult to apply for evolving media.

Another approach to ultrasonic monitoring is based on experimental rather than theoretical considerations. Ultrasound velocity and attenuation were found sensitive to a range of physical-chemical transformations (e.g., [2], [10], [11]). These experimental observations encouraged further phenomenological and empirical studies.

In this paper we discuss our observations on different methods of analysis of ultrasound signals propagating through chemically evolving aqueous solution, and compare the ultrasonic titration curve with the conventional pH one.

II. DESCRIPTION OF THE CHEMICAL PROCESS OBSERVED

The present study involves the titration of an aqueous solution containing Al^{3+} ions (sample) by the addition of hydroxide ions OH^- (titrant) in a similar fashion to our previous studies [12-13]. Simplified description of this process can be narrowed down to two main stages. Before the equivalence point at pH~7 the precipitate of aluminium hydroxide is gradually formed:

$$\mathrm{Al^{3+}(aq) + OH^{-}(aq) \rightarrow Al(OH)_3(s).} \qquad (1)$$

After the equivalence point the formation of aluiminate-ions $Al(OH)_4^-$ occurs:

$$\mathrm{Al(OH)_3(s) + OH^{-}(aq) \rightarrow Al(OH)_4^{-}(aq).} \qquad (2)$$

More rigorous description of the complex chemical processes involved can be found elsewhere (e.g. [12-13]).

The first overall reaction eventually leads to the formation of amorphous Al hydroxide which is quite common in nature (it can be found in soils, sediments, a number of minerals) and it finds numerous industrial applications in ceramics, as chromatographic phase, catalyst carrier, adjuvant, antacid, flocculant for water purification, etc. [14]. There have been indications in the literature that Al hydroxide can be an important source of toxic ionic forms of aluminium upon acidification of environmental waters [15,pp.110,455].

III. EXPERIMENTAL SETUP AND PROCEDURES

The measurement setup is shown in Fig.1 [16]. It contains the following analytical equipment: liquid handling unit (EDOS 5222, Eppendorf, **7** with replaceable tip **6**), pH meter (PHM-240, Radiometer, with pH electrode **5** and temperature probe **4**), magnetic stirrer **1** immersed into a solution under test **2**.

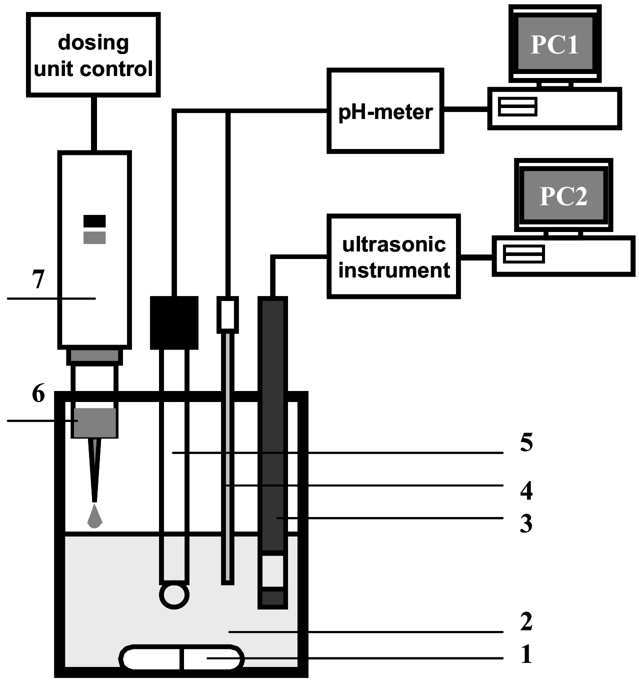


Fig.1. Experimental setup

The ultrasonic instrument (fig.1) contains the arbitrary function generator (NDT Solutions [17]) which integrated ultrasonic analogue front end (a pulser for excitation of ultrasound, and an amplifier for received signal), 8 bit digitiser with a sampling frequency of 320 MHz, and control unit with a PC interface. The ultrasonic probe **3** housed a 20 MHz ultrasonic transducer, and a reflector of incident waves [2,fig.47].

The monitored solution **2** initially contained 100 mL of $AlCl_3$ at 0.156 mol/L. Strong base (KOH at 2.863 mol/L) was added in 0.2 mL increments every minute [16]. Measurements (pH, temperature, ultrasonic parameters) were taken every 2 seconds. Both data acquisition and addition of reagents were conducted in a fully automated manner. No processing was applied to raw ultrasonic records in real time except amplification to fully utilise the dynamic range of an ADC. All the data were saved on a hard drive, and then batch-processed using custom written MATLAB subroutines. We plan to make both subroutines and data files publicly available from an anonymous FTP site.

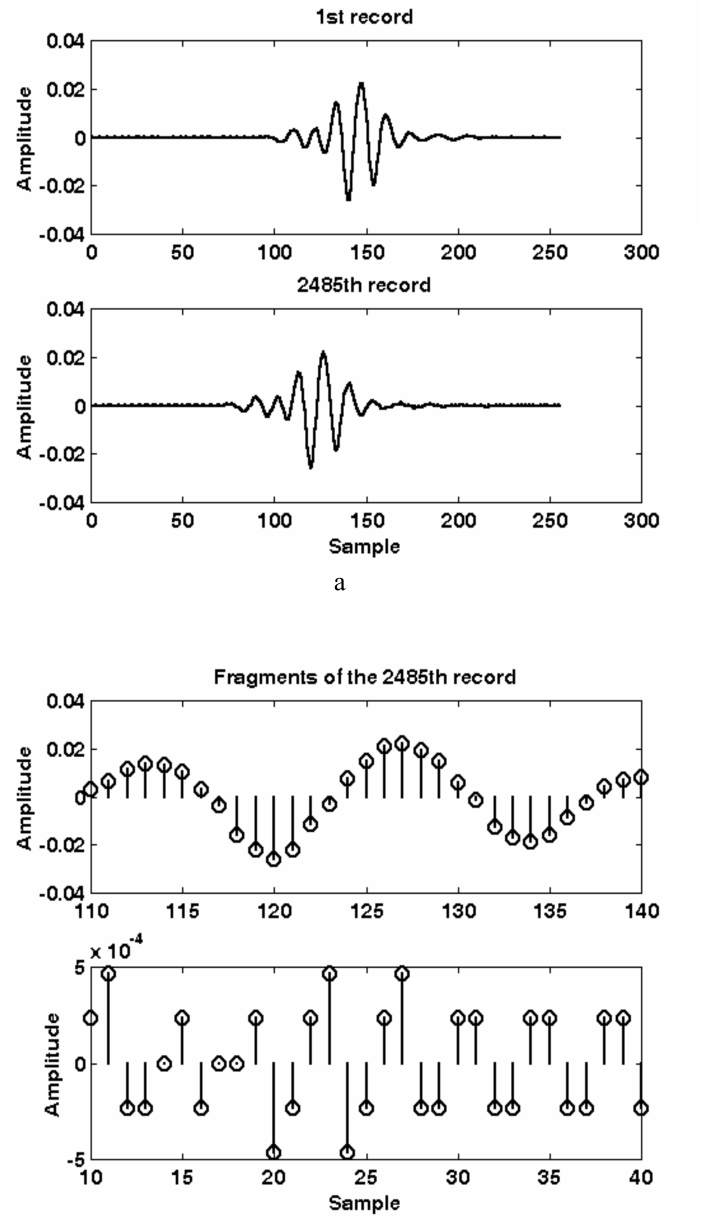
IV. SIGNAL PROCESSING PROCEDURES APPLIED TO THE EXPERIMENTAL ULTRASONIC DATA AND RESULTS OBTAINED

A. Pre-selection of records for analysis.

The first and the last records acquired are shown in fig.2. During the experiment we sometimes observed spontaneous appearance of air bubbles, mainly at times of the injection of the titrant, but sometimes due to entrapping some air at the surface of the sample solution due to powerful stirring (minimum 500 rpm). When these bubbles passed through the clearance of the ultrasonic probe, the received signal was distorted significantly. On top of that, additions of titrant to sample solution were released with some force that caused some hydrodynamic impact on the solution, and distortion of ultrasonic records as well. We used correlation analysis to filter out these odd records. If the correlation coefficient of any record with its predecessor was below 0.99, the record was excluded from consideration. This procedure resulted in exclusion of 109 records out of 2432 available per titrant addition (more than 4%). This is slightly more than what could be predicted based on drop statistics alone (one in every 30 records was affected by a drop that accounts for 3.3%). Fig.3 shows a set of calculated correlation coefficients. The vast majority of them are within the range of 0.993..0.998. The lower limit shows that the successive records are very similar indeed. The upper limit does not reach unity because of the influence of noise (mainly quantization noise as it is seen from fig.2b).

B. Visual inspection of records.

Comparison of the first and last records (fig.2) shows their apparent similarity. The recorded response retained both its shape and amplitude over the course of the experiment, the only notable change being a time shift of about 25 samples in the time domain. Automated extraction of a single (or few) parameters is required to obtain an ultrasonic titration curve that could be related to the chemical process observed. The measure selected (the parameter deduced from a raw record) should ensure good sensitivity to chemical changes and resilience to electronic noise as the noise could be magnified considerably depending on the measurement conditions [18].



a

b

Fig.2. The first and the last acquired records (a), and zoomed fragments of the last record (b)

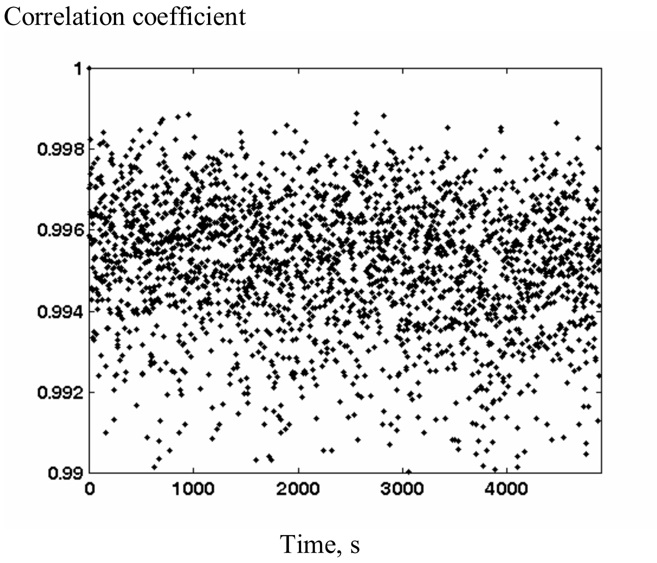


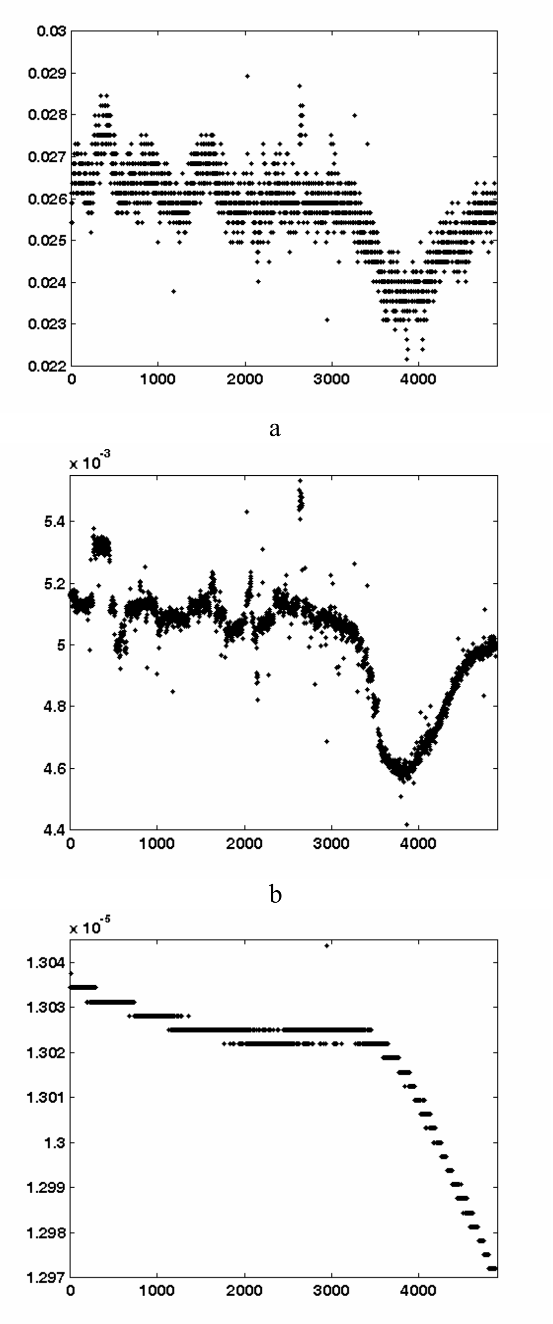
Fig.3. Correlation coefficients for pre-selected records

C. Time domain considerations.

Maximal amplitudes of the selected record set are presented in fig.4a. These data show the discrete nature of this measure due to quantization of the received signal, and a scatter of about 4% for neighbouring records, which is unacceptable. The standard deviation of a complete record was found more resolute and less scattered (fig.4b). It shows a steep decrease in the amplitude just before the equivalence point (down 10%), and its restoration when the aluminium hydroxide precipitate was then dissolved. This graph contains some spikes that seem not related to the process observed thus erroneous in spite of the pre-selection used. The spikes could be attributed to a situation when a small air bubble was formed on the surface of either transducer or reflector, and remained there for some time not affecting correlation coefficients of some records (temporary drop in amplitude). Alternatively, a bubble might collapse, but a new one could be formed instead soon (temporary increase in amplitude). The time position of every response could be estimated by the position of the sample with maximal amplitude (fig.4c). The graph shows a gradual decrease to a plateau that ends at the equivalence point, and close to a linear decrease afterwards.

D. Frequency domain considerations.

All the records were transformed into the frequency domain using the fast Fourier transform. The maximal amplitude among spectral components is presented in fig.5a, and resembles fig.4b. Less erroneous spikes were observed for the amplitude of the recorded signal at 20 MHz (nominal centre frequency of the transducer, fig.5b). The extent of change for both these graphs was close to 10% as for the standard deviation in the time domain. Fig.5c presents frequencies where the maximal amplitude spectral component was detected in every record. These data seem difficult to relate to the underlying process at all.



a

b

c

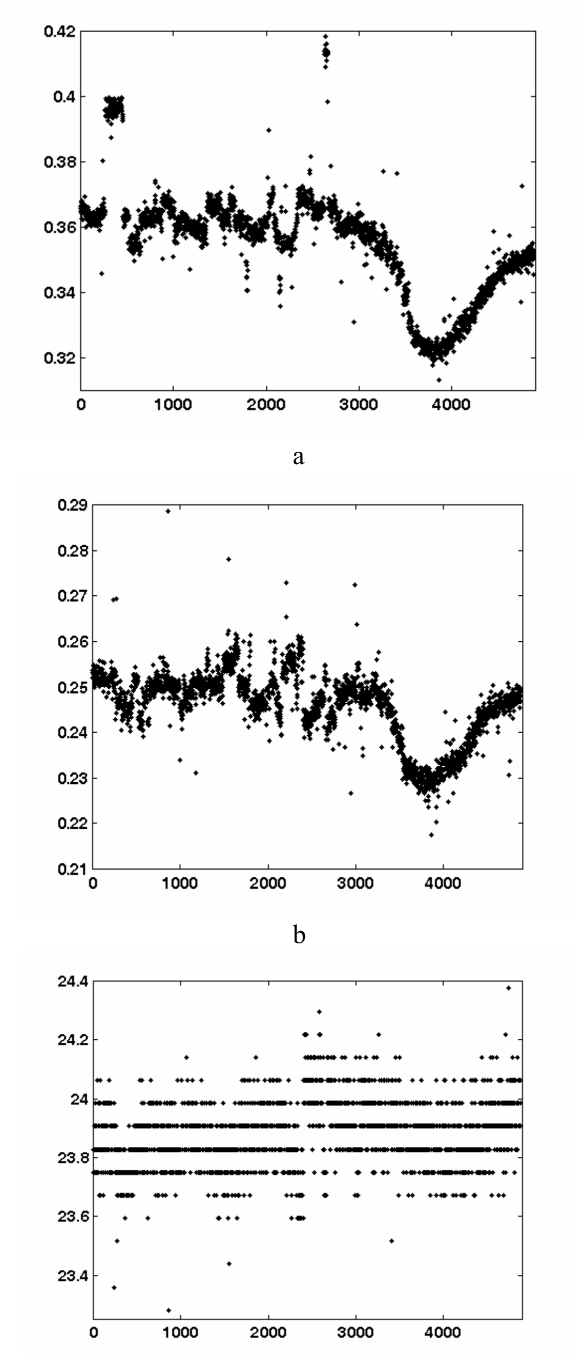
Fig.4. Time domain measures of the acquired record set (abscissa – time in seconds; ordinate – (a) maximal amplitude in a record, (b) standard deviation of a record, (c) time instant when the maximal amplitude occurred

E. Further elaboration of ultrasonic parameters for representing titration curves.

We identified time domain positions of the received pulses as the most promising measure based on the above analysis. This corresponds to group rather than phase velocity of ultrasound. However the hardware temporal resolution of the records was found to be a limiting factor. This resolution was improved by calculating the position of the centre of gravity (CoG) of the squared records:

$$CoG = \frac{\int t \times s^2(t)\, dt}{\int s^2(t) dt} = \frac{\sum n s_n^2}{\sum s_n^2}, \tag{2}$$

where $s(t)$ is the received signal, and s_n are its samples.



a

b

c

Fig.5. Frequency domain measures of the acquired record set (abscissa – time in seconds; ordinate – (a) maximal amplitude among spectral components, (b) amplitude at 20 MHz, (c) frequency of the component with the maximal amplitude

The obtained titration curve (fig.6) exhibits well separable clusters of CoG estimates on the right of the equivalence point. These clusters correspond to separate drops of the titrant [16]. Other techniques for enhancing temporal resolution could be used here, and we compared them with CoG by simulation. Techniques similar to CoG include centre of area [19] and centre of envelope [20] measures. A technique based on spline interpolation [21] was found similar to CoG in terms of sensitivity and noise resilience, but required more computing power. The above comparisons were made for a ratio of the transducer centre frequency to the sampling frequency of 16. However when this ratio was improved to 120 by using more resolute hardware, we found that use of the zero crossing technique was preferable [22]. We used exactly the same procedure that was described in detail by independent authors [23].

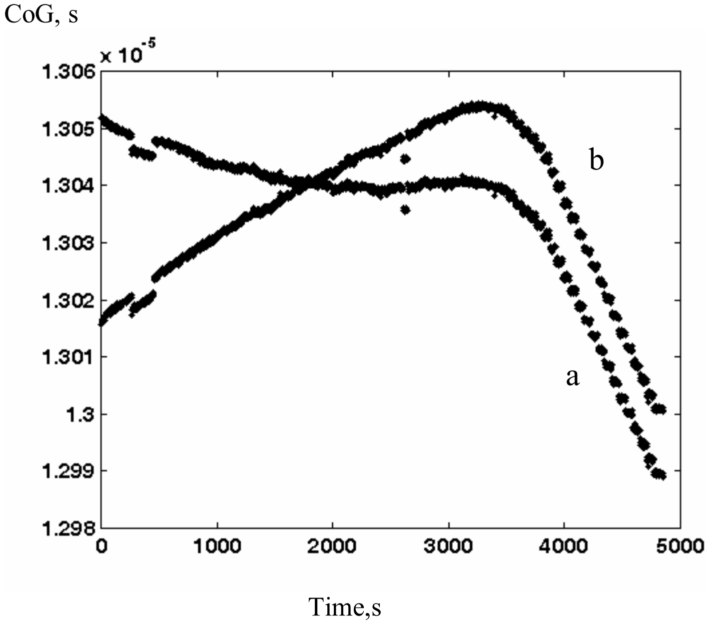


Fig.6. CoG titration curves before (a) and after (b) the temperature correction

F. Temperature compensation.

Acid-base titrations like the one we observed are exothermic. This could have lead to the observed temperature rise of 2.3°C. Ultrasound velocity is very sensitive to temperature changes, and we recalculated the CoG curve assuming the same dependence of ultrasound velocity in the observed solution as in water [22]. The corrected values are presented in fig. 6, and form two almost straight lines that intersect at the equivalence point. We believe this graph presents the most informative and convenient ultrasonic titration curve. (Temperature compensation can be accomplished based on ultrasonic records purely if an additional water-filled cavity is used [22].)

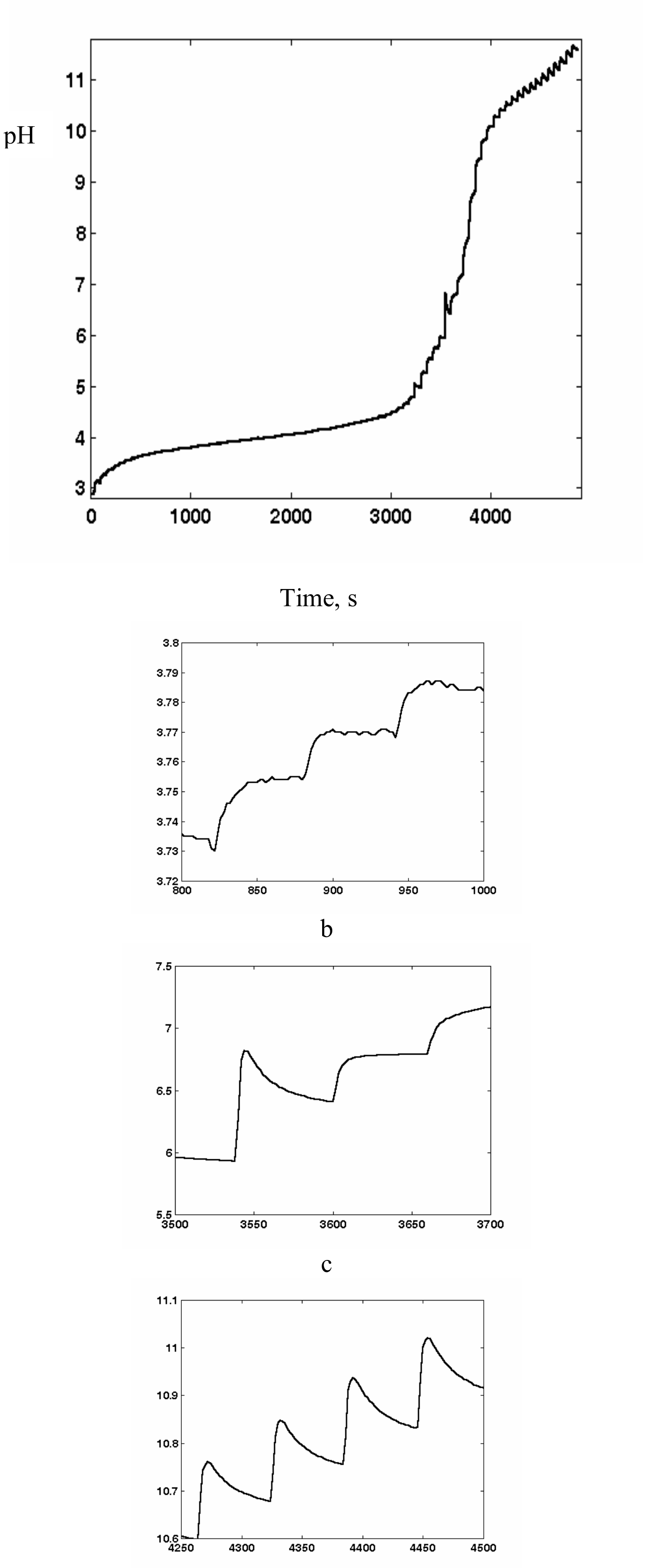
V. COMPARISON OF ULTRASONIC AND PH TITRATION CURVES

The recorded pH titration curve is presented in fig.7a and corresponds to a typical weak acid-strong base curve [1]. This curve is used to determine the equivalence point by detecting its intersection with some constant level of pH. Magnification of the curve shows that additions of titrant led to notable increases in pH (fig.7b-d). However the settling time was about 15-20 s in the acidic part of the curve, and more than that in basic conditions (pH>7, fig.7d). The time-resolved curve in the vicinity of the equivalence point (pH=7) exhibits a distinct shape (fig.7c).

In general, detecting (process monitoring) or holding (process control) an extreme value could be more convenient than doing the same with a numerical one. This is because in the later case frequent calibration is required to ensure the level is correct, while in the former case a constant offset or slight non-linearity could be tolerated. Another advantage of using ultrasound is the much smaller settling time that was estimated between 2 and 5 seconds. This time was primarily due to the stabilisation time of the reaction mixture itself.

VI. CONCLUSIONS

We applied different procedures to the set of ultrasonic data collected in the course of time-resolved weak acid-strong base titration. In the considered case the group velocity parameter was found the most noise resilient and sensitive to chemical changes. This conclusion is compatible with the observation of greater suitability of ultrasound velocity for study of intra- and inter-molecular processes [10]. Achieving resolution comparable to conventional analytical instruments requires the use of high sampling frequencies and advanced signal processing. The centre-of-gravity-based enhancement procedure was found appropriate for the reported experiment, but the zero crossing based procedure could be a viable alternative. Although most of the ultrasonic studies in aqueous solutions are conducted in a temperature-controlled environment, the possibility of a computational correction using independently measured temperatures (or obtained from the ultrasonic records purely) was successfully demonstrated *in situ.* Ultrasonic instrumentation showed significantly lower stabilisation times compared to the conventional pH meter.



b

c

d

Fig.7. Conventional pH titration curve (a) and its fragments (b-d)

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