

Oscillating bubble as a sensor of low frequency electro-acoustic signals in electrolytes

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2006 J. Phys.: Condens. Matter 18 7605

(<http://iopscience.iop.org/0953-8984/18/32/009>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 12:54

Please note that [terms and conditions apply](#).

Oscillating bubble as a sensor of low frequency electro-acoustic signals in electrolytes

N Tankovsky¹, K Baerner² and Dooa Abdel Barey²

¹ University of Sofia, Faculty of Physics, 5 James Bourchier Boulevard, Sofia-1164, Bulgaria

² University of Goettingen, IV Physics Institute, F Hund Platz 1, D-37077 Goettingen, Germany

E-mail: tank@phys.uni-sofia.bg

Received 13 October 2005, in final form 1 June 2006

Published 25 July 2006

Online at stacks.iop.org/JPhysCM/18/7605

Abstract

Small air-bubble deformations, caused by electro-acoustic signals generated in electrolytic solutions have been detected by angle-modulation of a refracted He–Ne laser beam. The observed electromechanical resonance at low frequency, below 100 Hz, has proved to be directly related to the oscillations of characteristic ion-doped water structures when driven by an external electric field. The presence of structure-breaking or structure-making ions modifies the water structure, which varies the mechanical losses of the oscillating system and can be registered as changes in the width of the observed resonance curves.

1. Introduction

The oscillating bubble/droplet techniques have been developed for experimental evaluation of viscosity and surface tension in different liquids and colloid solutions [1–3]. In these applications the resonance features of the oscillating bubble are registered and analysed. Thus the bubble is the active element, generating pressure changes in the examined solution. In the present work the air bubble is the passive, sensing element, responding by shape and size to the small pressure changes in the cell. The induced deformations of the bubble are registered optically with the help of a focused He–Ne laser beam. We are interested in the character of the driving electrostatic forces of interaction between a mobile electrode and charged particles (ions, dipoles, clusters) in the solution. The dynamics of the examined oscillating system is defined by the elasticity of the membrane, by the mechanical and electrical properties of the solvent and by the dynamical behaviour of the ions, when driven by the electric field to build an electrical double layer or when driven by diffusion to relax back to uniform density. The purpose of our measurements is to examine the electro-acoustic signals at low frequencies below 100 Hz, where the oscillating system is manifesting its main resonance, and to check the influence of different ions upon the characteristics of the resonance. The influence of cations and anions has been distinguished by applying dc voltages of different sign and value, thus separating the ions of different types in the vicinity of the electrodes. It has been shown that

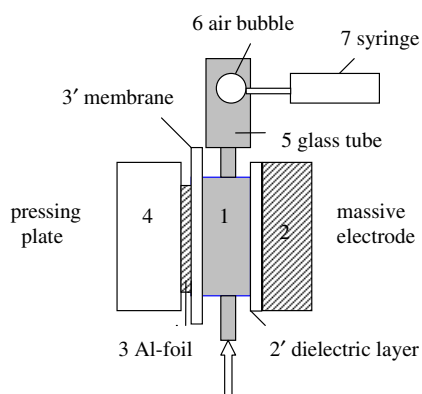


Figure 1. A scheme of the electro-acoustic-cell construction.

the resonance width, defined by the losses in the oscillating system, can reveal the influence of the ions on the structure of the solvent water.

2. Electro-acoustic cell construction and experimental set-up

The electro-acoustic cell construction is presented schematically in figure 1. The cell body is made out of Teflon, whereas the electrolyte solution is filled into the cell cavity (1), which is cylindrically shaped with diameter about 40 mm and interelectrode gap about 10 mm. The massive electrode (2) is made of aluminium alloy, isolated electrically from the solution by an Al_2O_3 layer (2') of thickness about $8 \mu\text{m}$, electrochemically deposited on the aluminium surface. The mobile electrode (3) is a thin aluminium foil, pressed on one side against a solid Plexiglas plate (4) and on the other side against a thin, stretched, elastic, latex membrane (3'), isolating the electrode from the solution. In this way the mobile electrode has a displacement freedom towards the solution and is constrained in the opposite direction. This scheme is in agreement with our hypothesis that mechanical oscillations occur when the mobile electrode is displaced into the solution, due to mutual attraction with the counter-ions, when an electric field is applied, and is pushed back by the elastic force of the membrane and by the hydrostatic pressure of the liquid when the electric field is switched off. The cell is filled with the examined electrolyte solution through an input opening, and is connected to a transparent glass tube (5). After the cell and the tube are filled with the solution, the opening to the atmosphere is closed by a valve. Finally, a small air bubble (6) (about 1–2 mm in diameter) is formed in the glass tube, at the opening of a capillary, by pumping a small amount of air through a syringe (7). In the so obtained closed cell (no connection to the atmosphere), the bubble is more stable and more shape sensitive to small changes of the pressure than in an open cell, when a free surface is present.

The experimental set-up for measuring the electro-acoustic signals, generated in the electrolyte solution, is shown schematically in figure 2. A generator (1) provides sinus-shaped electrical voltage, which is magnified by an amplifier (2) and is applied to the electrodes of the electro-acoustic cell (4). A power-supply (3) provides an additional dc voltage of different sign and amplitude to polarize the pre-electrode regions in the examined solution. The air-bubble (5) in the cell oscillates driven by the varying pressure generated by the displacements of the mobile electrode. The bubble responds to pressure changes by varying its shape and size, which can be probed with the help of a He–Ne laser beam (6), focused upon the bubble surface by a photo-objective (7). The refracted beam is angle-modulated and its intensity is

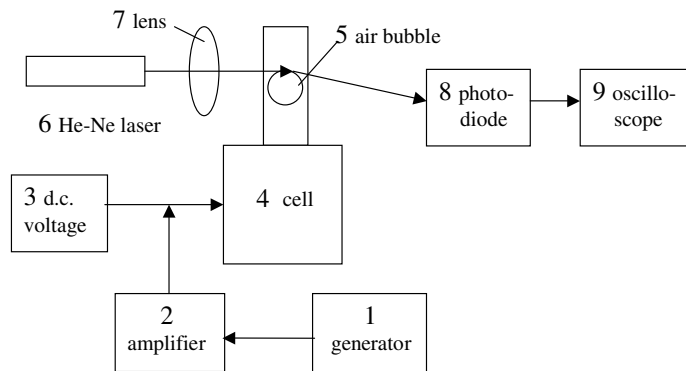


Figure 2. Block diagram of the experimental set-up.

registered by a photodiode (8). The obtained electrical signal is fed to a digital oscilloscope (9) for measurement and analysis.

3. Results and discussion

We have examined the frequency range 10–150 Hz, where the main resonance of the oscillating system, comprising the membrane and the adjacent layers of the solution, has been observed. The bubble, sensing the pressure variations in the liquid, is deposited well apart from the electric field, which is confined between the plates of the electrodes. We have noticed that the observed resonance characteristics are influenced by the electric field, but do not depend on variations of the bubble size. Moreover, it can be estimated theoretically that a bubble of the used diameter, 1–2 mm, has a lowest characteristic frequency f_0 in the order of a few kHz [4].

$$f_0 = \frac{1}{R_0} \sqrt{\frac{3K P_0}{\rho}}. \quad (1)$$

Here R_0 is the equilibrium bubble radius, ρ is the liquid density, P_0 is the hydrostatic pressure and K is the so-called polytropic index.

Hence we consider that the resonance observed at frequency below 100 Hz is not a bubble resonance. The general characteristics of the resonance curve—maximal amplitude frequency f_0 and resonance curve width Δf —proved to depend besides on the content of the solution and also on the sign and value of the dc electric field and on the stretching of the membrane. Thus the resonance can be attributed to the oscillating system in the membrane–solution region, where the electric field has its highest value, and not in the region of the surface of the oscillating air bubble.

The electrical signal amplitude of the photodiode depends on the optical adjustment of the probing beam: the incidence angle of the laser beam, the size and position of the focal spot and the size and shape of the bubble. A slow drift of the signal could be observed, due to variances of the bubble geometry caused by micro-leakage or small variances of the pressure in the solution. This is why optical tuning of the focusing system was performed for every measuring frequency point. As the maximal signal amplitude depends on the position of the focused beam spot on the bubble surface we have normalized the measured amplitudes to the maximal value. Thus the signal amplitudes are varying between zero and unity. Furthermore, we shall be interested mainly in the width of the resonance curves Δf , which is determined by

the losses (friction coefficient λ) in the oscillating system [5]:

$$\Delta f = \frac{\lambda}{2\pi}. \quad (2)$$

In our experiments we register the change of Δf when the sign and value of the applied dc voltage are varied. Thus the changes of Δf are attributed to the changes of the mechanical losses of the oscillating system, which prove to be informative on the local structure of the solution in the vicinity of the mobile electrode.

We want to distinguish the influence of the cations and anions in the obtained electro-acoustic signal, so we apply, besides the ac voltage, driving the oscillations, additionally a dc voltage. The massive electrode is active while the mobile electrode is connected to ground. Thus when a positive dc voltage is applied the membrane is polarized negatively and vice versa. In this way in the vicinity of the membrane (the oscillating system) either the cations or the anions have the dominant concentration, depending on the sign and value of the applied dc voltage. In order to avoid the eventual influence of adsorbed ions in the membrane we work with one membrane for the positive dc voltages and then change the membrane for the negative dc voltages. Small differences in the membrane stretching influence the resonance frequency f_0 . However, we shall be interested in the width Δf of the resonance curves, which is defined by the mechanical losses.

We have examined several aqueous solutions as follows.

- (1) We have started our measurements with pure, distilled water with a conductivity of about $0.05 \mu\text{S cm}^{-1}$. The occurrence of electro-acoustic signals in pure water might be explained either by impurities in the membrane, by dissociation of water molecules into ions OH^- and H_3O^+ , or by the electrical dipole of the water molecule. However, electro-acoustic resonance in pure water has been observed in the same frequency range with another cell construction, where the mobile electrode is floating on the surface of the solution and the sensing element is a droplet instead of a bubble [6]. Therefore, an eventual emission of ions from the membrane should be rejected as a main cause. The concentration of free ions OH^- and H_3O^+ is also extremely small. Moreover, both the free ions and the dipoles of the water molecules are not completely free. Instead, they are combined into clusters or associations building the characteristic structure of the water. For this reason we assume that the observed low frequency resonance is due to normal oscillations of the water structure in the vicinity of the mobile electrode. The presence of ions influences this structure, either enhancing the bonds (structure-making ions) or making the bonds weaker (structure-breaking ions). Different structures exhibit different mechanical losses and hence different resonance widths, which can be observed experimentally.

The spectra, obtained in distilled water, are shown in figure 3. The parameter Δf , measured for specificity at half-level, manifests some general properties in pure water:

- Δf is wider (bigger losses) when the membrane is negatively polarized as compared to the opposite case of a positively charged membrane. In this way the losses are higher when the concentration of H_3O^+ ions is high in the vicinity of the membrane (figure 3(a)), when compared with the losses pertinent to a high concentration of anions OH^- adjacent to the membrane (figure 3(b)).
- Δf grows wider when the applied dc voltage is increased in value. This can be explained by the fact that the electric field has an effect of decreasing the free motion of water molecules by orienting them along the direction of the field. However this tendency is better pronounced for H_3O^+ and is smaller for OH^- ions.

When assessing the role of the different ions for the losses of the oscillating system we shall keep in mind the fact that structured water is restricted by stronger bonds, which inhibits

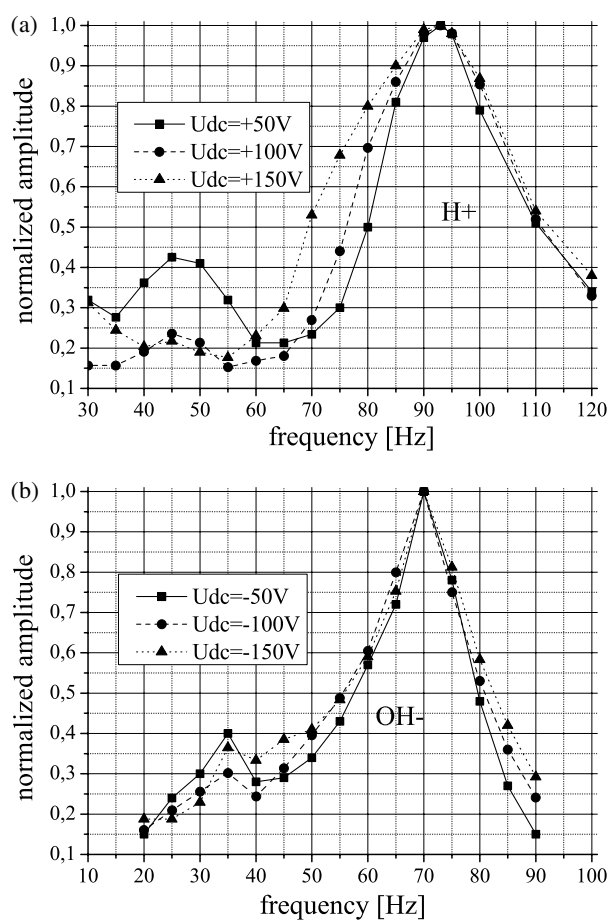


Figure 3. Electro-acoustic resonance curves in pure water: (a) negatively charged mobile electrode; (b) positively charged mobile electrode.

the free movement of the molecules, thus increasing their mechanical losses. In this way structure-making ions should have larger resonance widths than structure-breaking ions, which on the other hand support the free motion of the water molecules [7]. In this sense the experimental results show that the protonic ions H_3O^+ strengthen the structure of the water medium to a greater extent than the OH^- ions. This might be due to the increased number of H-bonds at higher concentrations of H_3O^+ ions.

- (2) The aqueous solution of LiI, concentration 0.005 M, gives us an opportunity to check the sensitivity of the experiment to variations in the water structure since the Li^+ cations manifest structure-making properties, while the I^- anions are structure-breaking ions [8]. The resonance curves are shown in figure 4 and they confirm our assumption that the observed electro-acoustic resonances are directly related to the structure of the solution. It can be seen that in the presence of the structure-making Li^+ ions (figure 4(a)) the oscillations have wider resonance curves and correspondingly larger losses than the curves in the presence of the structure-breaking I^- ions (figure 4(b)). We can also compare, besides the resonances of Li^+ and I^- ions, the resonance of Li^+ and H_3O^+ ions (figures 4(a) and 3(a)) as well as the I^- and OH^- ions (figures 4(b) and 3(b)). The losses of the solution in the presence of Li^+ ions are higher than in pure water at the same dc voltage. Hence Li^+ ions are better structure-makers than H_3O^+ ions. With the same

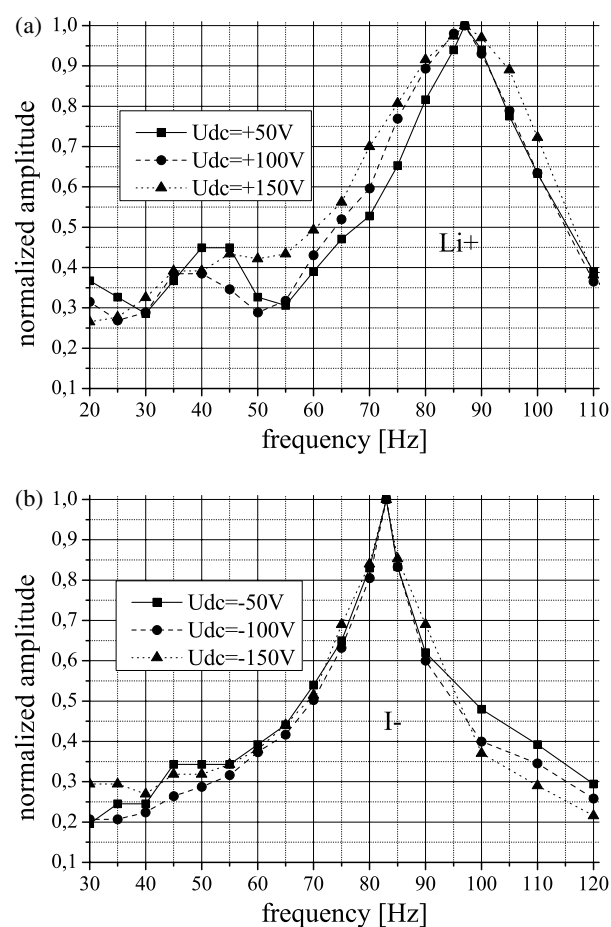


Figure 4. Electro-acoustic resonance curves in aqueous solution of LiI: (a) negatively charged mobile electrode; (b) positively charged mobile electrode.

logic we observe narrower resonances with I^- ions present, as compared to the resonance of pure water at the same voltage, i.e. in the presence of OH^- ions. This is in accordance with the qualification of I^- ions as structure-breakers, while the OH^- ions are known as weak structure-makers.

- (3) The next examined electrolyte is the aqueous solution of La acetate with a concentration of 0.005 M. The obtained resonance curves are shown in figure 5. It can be seen in figure 5(b) that at higher values of the dc voltage the acetate-pertinent curves are narrower than the OH^- curves, so acetate ions have stronger structure-breaking properties than OH^- . At low dc voltage, $U_{\text{dc}} = -50$ V, the resonance curve is wider for acetate $^-$ as for OH^- and I^- , which may be due to the presence of some La^{3+} structure-making ions in the vicinity of the mobile electrode. At higher dc voltages the polarization is stronger and the acetate ions are better separated from the La^{3+} ions, hence the curves become more narrow. The acetate ions, like I^- ions, have a large size and small charge and thus should be structure-breakers. Next, the La^{3+} cations (figure 5(a)) have a wider resonance than H_3O^+ at $U_{\text{dc}} = +100$ V, but a narrower resonance at $U_{\text{dc}} = +150$ V.

We can sort the ions in a descending order relative to their structure-making properties. The result is as follows:

$$\text{Li}^+ > \text{H}_3\text{O}^+ > \text{La}^{3+} > \text{OH}^- > \text{I}^- > \text{acetate}^- . \quad (3)$$

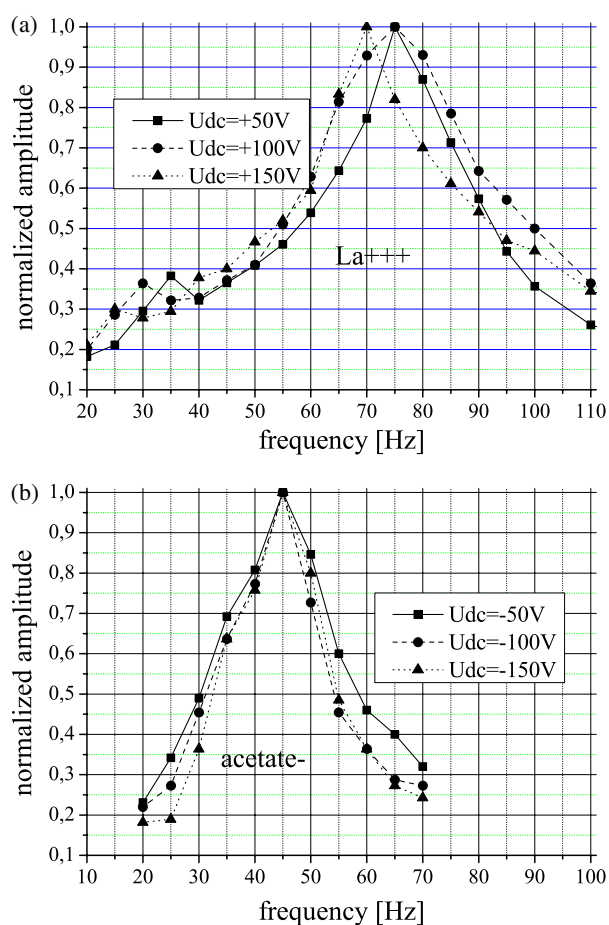


Figure 5. Electro-acoustic resonance curves in aqueous solution of La acetate: (a) negatively charged mobile electrode; (b) positively charged mobile electrode. (This figure is in colour only in the electronic version)

Table 1. Resonance half-widths Δf for different dc voltage and different ions.

U_{dc} (V)	OH^-	I^-	Acetate ⁻	H_3O^+	Li^+	La^{3+}
-50	23	28	27	—	—	—
-100	26	24	24	—	—	—
-150	28	26	23	—	—	—
+50	—	—	—	30	39	36
+100	—	—	—	34	42	45
+150	—	—	—	44	47	40

We have accepted sorting criteria in accordance with the highest applied value of the dc voltage, for which the separation of anions and cations in the vicinity of the electrodes is maximal.

In this sequence the position of H_3O^+ is justified as a strong structure-maker due to the H-bond, while OH^- is a very weak structure-maker.

Finally, the obtained results are shown in table 1:

It can be noticed that the cations manifest more pronounced structure-making properties in comparison with the anions. The resonance widths of the oscillations related to the structure-breaking ions I^- and acetate⁻ become smaller when the dc voltage is growing, opposite to the

resonance widths of structure-making ions, which become larger when the dc voltage grows. This may be explained with the increased local concentration of the given type of ions when the polarizing dc electric field gets higher.

Two other interesting peculiarities can be observed in the obtained results. Firstly, the resonances obtained in the presence of structure-making ions, figures 3(a), 4(a), 5(a) and 3(b), manifest parametric nonlinearity; i.e., besides the main peak at frequency f_0 a smaller peak at frequency $f_0/2$ can be observed. Such nonlinearity is not observed in the resonances of the structure-breaking ions (figures 4(b) and 5(b)). Secondly, the resonances in the presence of the structure-making ions are broadened asymmetrically when the dc voltage is increased, whereas the main resonance is skewed towards the sub-harmonic. Moreover, it seems that energy is transferred from the sub-harmonic to the main resonance since the asymmetric broadening of the main resonance is accompanied by decrease of the amplitude of the sub-harmonic. It can be noticed that the nonlinear evidence in the resonances for the different ions roughly decreases in the same gradation as the decreasing gradation of the structure-making properties of the ions, as presented in series (3). Thus, the mentioned peculiarities of the resonances can be attributed to the nonlinear properties of the water structure, modified by the presence of the different ions.

4. Conclusions

A method is suggested to define experimentally the influence of different ions upon the structure of the solvent water, based on the measurement of the mechanical losses of the oscillating system: elastic membrane-adjacent solution, when driven by an ac electric field. Dc electrical fields of different signs and values are applied additionally to polarize the electrodes and thus separate the influence of cations and anions in the vicinity of the oscillating membrane. The obtained results are in qualitative agreement with the general knowledge about the influence of different ions on the structure of water. However, an improved precision of the data is advised. One possible alternative implementation rests on the use of a piezoresistive pressure sensor. This would eliminate the unstable optical adjustment and signal drift, which is often observed. In principle, the knowledge of the structure-breaking or structure-making properties of ions in solution could be used to estimate the energy of interactions between the water molecules and the hydrated ions. Measurements at different temperatures would also shed some light upon the electrolyte structure, in particular close to the ice point.

Acknowledgment

One of the authors, NT, gratefully acknowledges support by the Alexander von Humboldt foundation.

References

- [1] Kovalchuk V I, Kraegel J, Aksenenko E V, Loglio G and Liggieri L 2001 *Novel Methods to Study Interfacial Layers* (Amsterdam: Elsevier Sciences) pp 485–520
- [2] Wantke K D and Fruhner H 1998 *Drops and Bubbles in Interfacial Research* (Amsterdam: Elsevier) pp 327–65
- [3] Plesset M S 1997 *Annu. Rev. Fluid Mech.* **9** 145–85
- [4] Minnaert M 1933 *Phil. Mag.* **16** 235–48
- [5] Landau L and Lifshits E 1988 *Theoretical Physics, v.1 Mechanics* (Moscow: Nauka) (in Russian)
- [6] Tankovsky N, Nikolov I, Buchvarov I and Baerner K 2002 *J. Appl. Phys.* **92** 7180–2
- [7] <http://www.aquatechnology.net>
- [8] Krestov G A *et al* 1987 *Ion Solvation* (Moscow: Nauka) (in Russian)