



Photoacoustic determination of speed of sound in binary mixtures of water and ethyl and methyl alcohol



P. Pardini^{a,*}, D.I. Iriarte^a, J.A. Pomarico^a, H.F. Ranea-Sandoval^b

^a IFAS – CIFICEN (UNCPBA – CONICET), Pinto 399, 7000 Tandil, Argentina

^b IFAS, UNCPBA, Pinto 399, 7000 Tandil, Argentina

ARTICLE INFO

Article history:

Received 16 April 2015

Accepted 12 November 2015

Keywords:

Speed of sound

Photoacoustics

Binary mixtures

ABSTRACT

The speed of sound in binary aqueous solutions of two alcohols by means of the pulsed photoacoustic technique has been determined. Hereby an analysis of the relationships of excess thermodynamic properties of the mixture to the speed of sound in it is presented. It is also shown that neither the Grüneisen coefficient nor the absorption coefficient of the mixtures are additive functions of the composition. The advantage of this method of speed determination lies in its inherent simplicity and the good precision attained. It can be used in tomography of water in different phantoms and potentially in tissues of biological origin.

© 2015 Elsevier GmbH. All rights reserved.

1. Introduction

In this work we report the measurement of sound speed in several binary aqueous mixtures with two simple alcohols, by means of the NIR pulsed laser photoacoustic technique, and the direct determination of the absorption coefficients of such mixtures by a spectrophotometer determination. We have investigated the possible variations of the elastic properties that could account for the precise dependence of the sound velocity on the thermodynamic excess properties arising from the interaction between water and alcohol molecules through hydrogen bonds.

Recently, a new application for photoacoustic tomography has been presented, namely the tomography of water in biological tissues [1]. This procedure successfully applies the capabilities of the photoacoustic technique to the detection of water in the NIR, extending the range of utilization to the high resolution mapping of water. This work was based in a previous proposal [2] where the analysis of this type of matters began with mixtures of water and ethyl alcohol in order to vary the absorption of the inhomogeneities inside phantoms used to simulate irregularities in tissues. From another point of view, [2] poses an interesting question about the amplitude of the maximum of the PA signal in mixtures containing water. The authors imaged water–ethanol and pure water inclusions in gel and water inclusion in fat tissue; the significant difference in photoacoustic signals between water and fat tissue

indicates that the laser-based photoacoustic tomography is potentially capable of detecting water content in different tissues.

In fact, we study whether the speed of sound is an additive function of the mixture composition, and if its corresponding absorption coefficient or the rest of the mechanical and thermal parameters are additive too. These are the parameters involved in the determination of the peak of the generated acoustic signal, according to the current theoretical models [3]. There is a potential area of interest for mixtures of liquids: the analysis of the effects of water in the thermodynamics of mixtures, and thus in the detection of presence of localized aqueous mixtures in an otherwise homogeneous sample.

The determination of the speed of sound in certain media is of interest in several research areas. In Biomedicine it can be used for calibration and assessment of quality of the ultrasound imaging techniques; in Engineering it is used in the analysis of the products that contain water and alcohols and its applications as solvents and co-solvents; in Chemistry it is also possible that this method can contribute to bring information about certain thermodynamics properties of mixtures and of the changes of structure of different mixtures as well.

Our results were compared to the results of a variety of techniques for measuring sound speed in mixtures, rendering similar values.

Other photoacoustic-based systems for studying the propagation in tissues and in phantoms are shown, for example, in [4] where a prototype of laboratory photoacoustic mammography system is presented, based in the plane-parallel geometry, working in NIR using a novel poly(vinyl alcohol) gel phantom. In [5], the content of glucose and its influences in the signal in Intralipid®

* Corresponding author. Tel.: +54 2494385660.

E-mail address: ppardini@exa.unicen.edu.ar (P. Pardini).

and in pig-blood liquid phantoms is studied by photoacoustic techniques based in Nd:YAG laser in its two emission lines. In [6] the studies of in vitro and in vivo samples are presented. These were conducted in order to explore the factibility of the photoacoustic technique as a spectroscopic tool for non-invasive determination of glucose in blood.

The use of NIR Nd:YAG laser in [7] demonstrates that there are areas which can be inspected by these lasers, as in the decreasing amplitude of the photoacoustic signal in a sequence of pulses in dental enamel treatment, and in chicken and turkey breast. In [8] a review of the applications of this technique in image diagnosis is presented, in imaging and in intra-arterial therapy, monitoring of brain oxygenation, and in glucose level determination in blood, together with several studies on the eye's layers and diagnosis of breast cancer systems. In fact, the photoacoustic technique could be used to image organs or as a complement of other inspection systems as those using light transport in turbid media, by diffusion [9,10].

Now, in order to achieve precision in this mapping, there has to be a precisely measured speed of sound in normal conditions as well as in those affected by well-defined edges irregularities or those with less localized lesions, tumescence or tumors. On the other hand, in other type of analysis it is important to know with precision the optical properties of the media of interest, to which the photoacoustic technique could help, providing, for instance, the absorption coefficient, of relevance in the Biomedicine or in other fields of industry as well.

The determination of the speed of sound in aqueous liquid mixtures was done, for example, in [11,12] by means of a velocimeter in which the sound had a fixed path, and also using an instrument consisting of an interferometer of variable path. In both cases, the frequency was fixed and the determination of the wavelength allowed evaluation of the sound speed with good level of correlation between both methods. In [13] the speed of sound in binary mixtures of water and ethanol was evaluated counting several wavelengths by a standard phase-comparison method. There, a variable path cuvette was immersed in a thermostatic bath and taking a distance, ranging from 50 to 250 wavelengths, a further determination of the frequency brings the speed of sound. In [14] this measurement was done using the Brillouin scattering of a polarized laser and comparing it with a velocimeter using ultrasound pulses traveling through a known path length container, and determining the time of flight of the pulses.

It is common-knowledge fact that the mixtures of water and several alcohols exhibit thermodynamic properties in excess that are consequences of structural coordination of the molecules of the polar liquids involved. A manifestation of this is that a property, such as the volume, is not additive in the sense that the volume of the mixture is not the added volumes of the components, and this holds true for the heat capacity, the elastic constant, the thermal expansion coefficient and even for the absorption coefficient; thus, the speed of sound is not additive in that sense, since it is related to mechanical properties like the bulk compressibility, and the density. The heat released in the photoacoustic effect is also affected by the volume contraction consequences, and thus the prompt heat dissipation photoacoustic signal will be also affected non-additively.

We present here the measurement of the speed of sound in aqueous mixtures by means of a direct photoacoustic detection by a PZT pickup in a pulsed laser system, and the influence of the non linear dependence of the parameters involved in it. We did not find this method described here in the previous literature of speed of sound determination, applied to these particular mixtures or the analysis on the additivity issues. We use this technique since it can be applied to some extent either to biological samples in vitro or in vivo, that is in real-time, or to other type of samples, such as

liquids mixtures, synthetic or semi-synthetic solids. The advantage of using this technique lies in its simplicity in data acquisition, in the interpretation of the results and in the experimental setup. We shall show that the determinations made by this procedure are sufficiently accurate as to compare well with other, more sophisticated apparatus like those cited before.

We present also a consistent set of values for the Grüneisen coefficient acquired from the measurement of the mentioned speed of sound and an accurate set of data for the heat capacity and the thermal expansion coefficient of the mixtures used taken from [15,16], together with the already mentioned direct measurements of the absorption coefficients of the mixtures. We are convinced that these results could be interesting for the quantitative determinations of water in different contexts, especially in the photoacoustic tomography of water, in Bio-medical samples.

2. Experiment description

The measurement of the speed of sound was done using a well-known direct laser photoacoustic detection setup [3]. It is schematically represented in Fig. 1. The pulsed laser was a Q-Switched Nd³⁺:YAG working at the 1.06 μm wavelength with a pulse duration of approximately 10 ns, and set at a pulse repetition frequency of 10 pps. The beam impinged in a face of a square glass spectrophotometer cuvette 10 mm optical path, the liquids samples filled it. At the faces at right angles to that one hit by the laser pulses a C-clamp that pressed both faces, at one, a square, 4 mm PZT transducer, that was mounted in a 10 mm cylinder steel cage with suitable conditioning. The C-clamp served as to push the PZT against the cuvette for acoustic impedance issues. During the whole set of measurements, the cuvette, once was properly aligned, remained untouched, and the liquids were poured carefully into it in order to avoid both bubbles and mechanical perturbation of the setup.

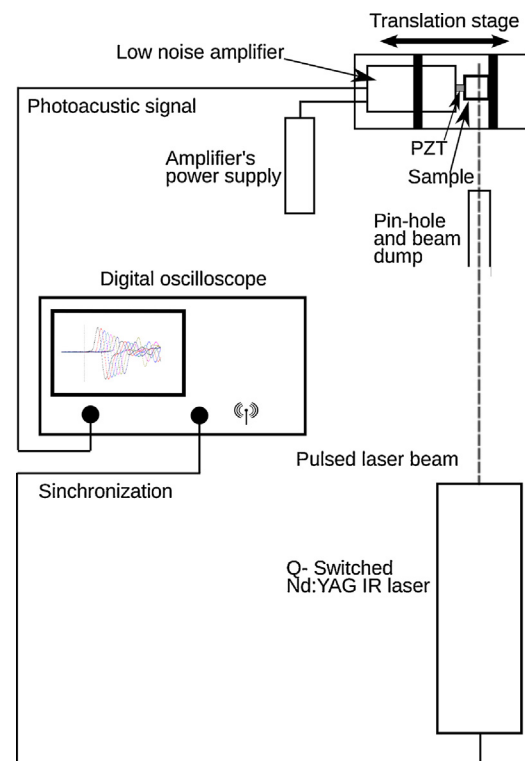


Fig. 1. Experimental setup. The description of each item is in each box.

The liquids studied were obtained for the three combinations of the above mentioned liquids: distilled water (DW) and ethyl alcohol (EtOH), DW and methyl alcohol (MeOH) and EtOH and MeOH. Eleven mixtures for each of the binary combinations were made, varying the composition in volume steps of 10% that were afterwards converted to molar fractions. The speed of sound was determined for each of the total of 33 samples.

The laser was not focused onto the samples, instead, a pin-hole drilled in a 0.5 mm stainless steel plate was used to reduce the beam diameter from the original 6 mm to approximately $350 \pm 10 \mu\text{m}$. For operator's security reasons, the metal pin-hole was mounted at the end of an aluminum tube in order to dump the reflected laser beam. The detection scheme was completed by an amplifier following the output of the *PZT* that ensured good *S/N* ratio and sufficient bandwidth as to allow the signal to be well-reconstructed specially at the beginning, where data for sound speed was taken. The amplifier was developed at Centro de Investigaciones Ópticas (CONICET-CIC) of La Plata-Argentina in the Research group directed by Dr. G. M. Bilmes.

The samples were excited by this near-cylindrical beam which, by absorption in the liquids, generates a cylindrical pressure-wave which in turn originates, by the photoacoustic effect, the acoustic wave detected at the transducer. Hence, there should be a delay between the laser firing and the arrival of the wave at the acoustic detector, which is mainly due to the speed of sound in the sample. Knowing this delay for different relative positions of the point of laser impinging to the detector, provided the system is correctly aligned, brings the searched speed of sound with good accuracy.

The cuvette was mounted on a plate having manual micrometric horizontal displacement system as to vary the distance between the source and the detector, i.e. r , with a precision of $10 \mu\text{m}$ and a total displacement of approximately 20 mm, although roughly 8 mm were enough to scan the useful part of the sample. The temperature of the liquid was monitored by a digital thermocouple thermometer, and only the data produced at a range of less than $\pm 1^\circ\text{C}$ off the ambient temperature was considered for this work.

Times of arrival of the sound pulse to the detector were evaluated from the “foot” of each of the signals in different ways, i.e., taken de time where de signal takes 1, 5 and 10% of the peak, and the values found for the speed were always consistent with our experimental error of the order of 1%. The distance between source and detector was calibrated with a precision of 0.5 mm. The analysis and storage of the signals was done by a 300 MHz Tektronix TDS 3032B digital oscilloscope, averaging 64 sampled signals. The rest of the data analysis was done by means of a personal computer and Open Access software.

In order to illustrate the evaluation of the speed of sound, we show in Fig. 2 how is this accomplished, in the case of distilled

water (DW). The part (a) displays photoacoustic signals taken for different values of the distance between the detector and the laser beam (r), and arrival times (t_r) are measured from the point marked as 0, a vertical dashed line in the figure. In the part (b) of Fig. 2, the time-delay is represented vs. r . The experimental points were then linearly fitted to a straight line, setting the sound velocity as the inverse of the slope of the linear fit.

From Fig. 2(b) the speed of sound is obtained for the sample DW from the fitting, since b is the slope of the straight line, using

$$t_r = br + t_{r0}; \quad t_{r0} = 0; \quad v = \frac{1}{b} \pm \frac{\Delta b}{b^2}. \quad (1)$$

From the data, the speed of sound in the sample used for the construction of Fig. 2, was determined with an uncertainty of 0.90%.

Other parameters were determined by auxiliary measurements. The mixtures were prepared by means of graduated instruments with precision enough to be repetitive in the results that are condensed in this work. The absorption coefficients for the mixtures used in this paper were measured using a Shimadzu spectrophotometer Model UV-1800, and the diameter of the pin-hole was determined by a calibrated digital microscope by National Optical Scientific Instruments, Model DC5-420 TH.

The maximum of the photoacoustic signal shown in Fig. 2(a) follows the model proposed by Tam:

$$S_{PA} = K \frac{\alpha \beta v^2}{\pi C_p r^{1/2} R^{3/2}} E = K \frac{\alpha \Gamma}{\pi r^{1/2} R^{3/2}} E, \quad (2)$$

and is called thick-cylinder approximation. It depends on the characteristics of the experimental setup: r the distance between the optical excitation and the acoustic detection, R the radius of the excited cylinder, i.e. the diameter of the laser, E the energy of the laser pulse, and K the combined *PZT* and a mechanical conversion constant dependent on the particular arrangement used to hold the sample. The other parameters depend on the characteristics of the studied sample, so it is extremely important to keep the arrangement unchanged for the whole set of experiments in order to make comparisons of signal amplitudes and other sources of errors coming from positioning and holding the cell.

As the maximum of the prompt-heat dissipation signal is proportional to the product of the absorption coefficient α and the Grüneisen coefficient Γ , these are interesting parameters that were also analyzed. The latter is a dimensionless parameter related to the speed of sound v , the thermal expansion coefficient β , and the heat capacity C_p , expressed by $\Gamma = \frac{\beta v^2}{C_p}$.

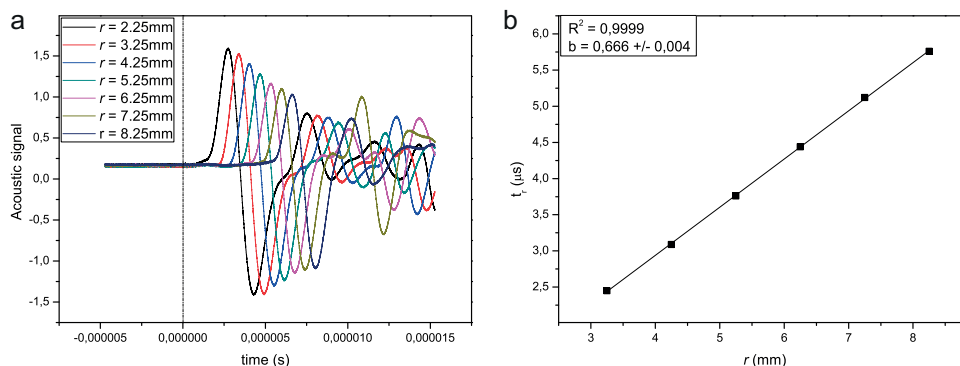


Fig. 2. (a) Acoustic signals in distilled water (DW) for different relative positions of *PZT* and laser beam for distilled water. (b) Experimental points t_r vs. r taken from the signals in part (a) and the linear fitting line. The $R^2 = 0.9999$ of the line allows a slope b determination $b = 0.666 \pm 0.004$.

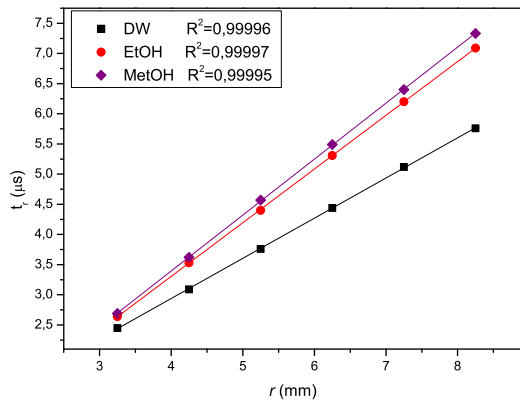


Fig. 3. Fitting of points t_r vs. r , for distilled water (DW), ethyl alcohol (EtOH) and methyl alcohol (MetOH).

3. Experimental results

In Fig. 3 we display the results of the measurements of the speed of sound in the three liquids: DW, EtOH and MetOH. These are the liquids that were used to make the binary mixtures by combination. There is an excellent linear relation that fits the data points, since in all cases $R^2 \geq 0.99995$, which assures a speed uncertainty of less than 1.2%.

From these straight lines, we can calculate from Eq. (1) the speed of sound in the pure liquids samples. The values for that variable are: $1501 \pm 9 \text{ ms}^{-1}$ for DW, $1149 \pm 9 \text{ ms}^{-1}$ for EtOH, and $1052 \pm 8 \text{ ms}^{-1}$ for MetOH.

Fig. 4 summarizes the results of the measurement of the speed of sound for each of the binary mixtures vs. its composition. The two cases of aqueous mixtures are displayed as compared to the speed of sound measured by various other authors (references are indicated in the figure, the methods used are by means of the velocimeter by Onori et al., and Brillouin scattering by Mijakovic et al., both described in Section 1), being the consistency between our results with those of the references reasonably good. Since we could not find values in the literature for the third mixture (EtOH with MetOH) we report the results separately. The results thus confirm others with a very simple experimental setup.

In the case of the DW/EtOH mixture all the values shown for the speed of sound are within the experimental error of the authors cited. The percentage differences with the values reported by the references cited are not greater than 2.5%. For the mixture DW/MetOH the values are also within the experimental error of the references, except solely for pure MetOH for which our value and the reference value are an 7% apart, which is attributable to

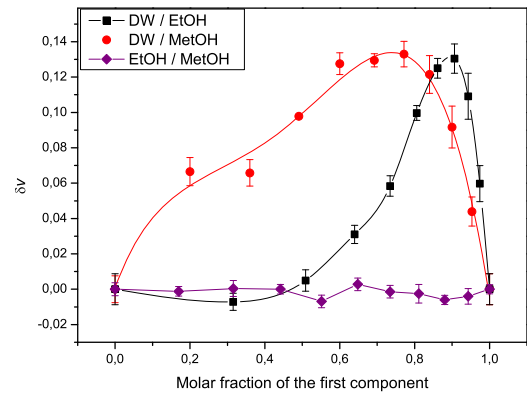


Fig. 5. Experimental values for the speed of sound compared to the additive speed through the parameter δv vs. the composition of the mixture, for distilled water and ethyl alcohol (DW/EtOH), distilled water and methyl alcohol (Met/OH), and ethyl alcohol and methyl alcohol (EtOH/MetOH).

differences in the composition of the reagent MetOH used in our case.

Our results for the combinations of DW/EtOH, in turn, have experimental discrepancies between 0.5% and 1.2%; for the DW/MetOH the uncertainty lies between 0.4% and 1.1%. Finally, for the case EtOH/MetOH the band of uncertainty lies within 0.3% and 0.6%, in the whole range of compositions (see error bars in Fig. 5).

The peculiar shape of the change of the speed of sound with composition differs with the one that would be sensible if it were not for the thermodynamic excess of the parameters involved in this propagation speed. The additive speed should be

$$v_{ad} = x v_1 + (1 - x) v_2, \tag{3}$$

where x is the molar fraction of the first component and v_1 the speed of sound corresponding to such component, and $(1 - x)$ is the molar fraction of the second component, being v_2 the speed of sound for that component if pure.

The excess of speed of sound that can be determined by the relation between the speed of sound corresponding to the measured (suffix “meas”) and the one that comes from Eq. (2) relative to the additive one (suffix “ad”) is

$$\delta v = \frac{\Delta v}{v_{ad}} = \frac{v_{meas} - v_{ad}}{v_{ad}}. \tag{4}$$

From Fig. 5, in the case of aqueous solutions, the curve representing δv is polynomial in shape, displaying a maximum at molar fractions near unity ($\delta v \sim 0.9$ for DW/EtOH, and approximately $\delta v \sim 0.85$ for the DW/MetOH). Instead, for the EtOH/MetOH mixture, the curve for δv is nearly horizontal, indicating that the speed of sound is approximately additive.

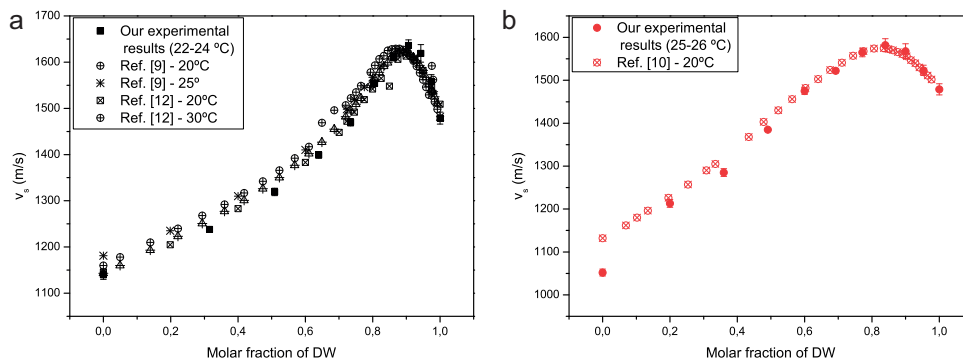


Fig. 4. Speed of sound vs. molar fraction of distilled water (DW) determined by the photoacoustic method for aqueous mixtures with: (a) ethyl alcohol, (b) methyl alcohol, compared with the authors of the references cited in the inset of the figures (see also Reference section) at temperatures similar to the ones of this work.

4. Discussion of results

The different values for the speed of sound measured to those evaluated by the additive expression, can be related to the already mentioned thermodynamic properties in excess to the additive ones.

Fig. 6 helps comparing the percentage thermodynamic properties in excess, related to the speed of sound measured here. The properties displayed are the percentage changes in bulk compressibility coefficient K , and in the density ρ , together with the percentage change in speed of sound, since these are the properties directly related to the velocity of sound in

$$v = \sqrt{\frac{K}{\rho}}. \quad (5)$$

In Fig. 6 the excess in the three related functions of the composition for: (a) the binary mixture of distilled water and ethyl alcohol, and in (b) the mixture distilled water and methyl alcohol. The excess for the speed of sound shows a maximum at the maximum of the elastic properties displayed.

From Eq. (5), we can evaluate the excess in these parameters since at first order we have

$$\frac{\Delta v}{v_{ad}} = \frac{1}{2} \left(\frac{\Delta K}{K_{ad}} + \frac{\Delta \rho}{\rho_{ad}} \right), \quad (6)$$

where again, the suffix “ad” stands for additive property and is calculated according to the Eq. (3) shown before; here, the symbol Δ indicates the excess in each parameter. In this estimation, the data for the elastic properties and density are taken from [11,12,17] respectively, while the data for the speed of sound comes from our work. This estimation is also shown in Fig. 6.

Although the liquids used in this work and the temperature at which experiments were done are not exactly those used in the references from which we obtain certain mechanical properties, there is a very good agreement between the speed of sound measured by us and that evaluated from the data. Thence, the study here presented strongly suggests that the speed of sound variation with the composition of the mixtures is clearly related to the thermodynamic excess properties of the mixture.

In Fig. 7, the speed of sound in aqueous binary mixtures is compared to the excess in other thermodynamic properties involved in the generation of the photoacoustic signal: the ones related to the Grüneisen coefficient and the absorption coefficient, and also the density.

All the properties shown, including not surprisingly the absorption coefficient α , have an excess maximum for higher molar fractions of water. Since these excesses are related to structural changes in the solution, it is expected that all shall peak at approximately the same molar fractions values. They do not exactly coincide with the maximum variation for the speed of sound found in this work; however, they are in general agreement with it. The temperatures of the mixtures in this work were not precisely the ones we choose for comparison with other results, they are at most 5 °C apart and there is no evidence that this difference is substantial to change any of the conclusions we present here.

By determining v , and using data in Refs. [15,16,18] we have been able to estimate the Grüneisen coefficient, Γ . First, we estimated its value by using the properties with their excess, and then, we compared it with the value estimated using the additive properties, calculated as the additive velocity in Eq. (3). Finally, we obtained the difference of the Grüneisen coefficient estimated with excess properties (suffix “exc”) and with additive ones (suffix “ad”), as

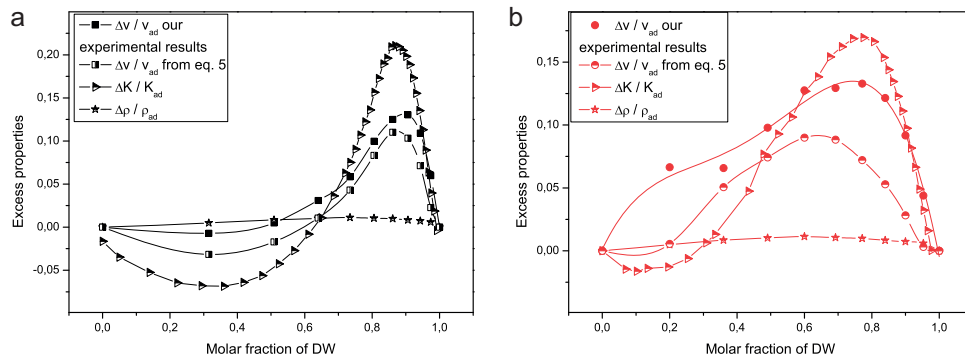


Fig. 6. Excess compressibility, density, and speed of sound (measured and estimated from Eq. (5)) vs. composition of the mixture: (a) for distilled water and ethyl alcohol (DW/EtOH), (b) for distilled water and methyl alcohol (DW/MetOH). Data re-elaborated for compressibility coefficient K , from Onori et al. [11,12], and density ρ from CRC Handbook [17].

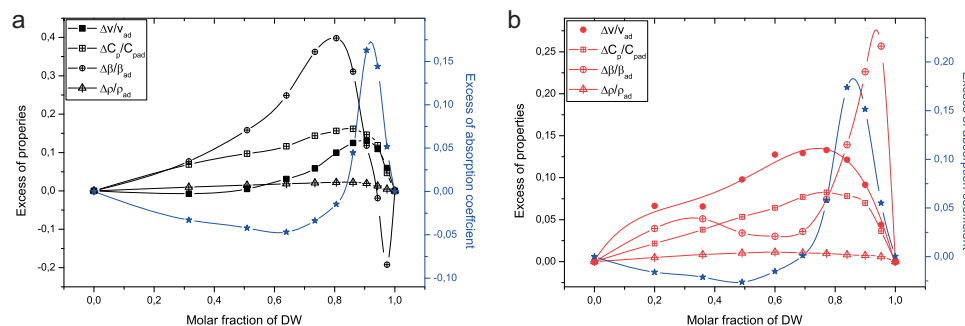


Fig. 7. Relative excess in all the parameters involved in the generation of photoacoustic effect (according to the model developed in Ref. [3]): v , speed of sound, determined in this work; C_p , isentropic heat capacity, re-elaborated from: [16]; β , isothermal expansion coefficient, re-elaborated from [15]; α , optical absorption coefficient, determined in this work; and ρ , density, re-elaborated data from [17]. Part (a): distilled water and ethyl alcohol (DW/EtOH); part (b): distilled water and methyl alcohol (DW/MetOH).

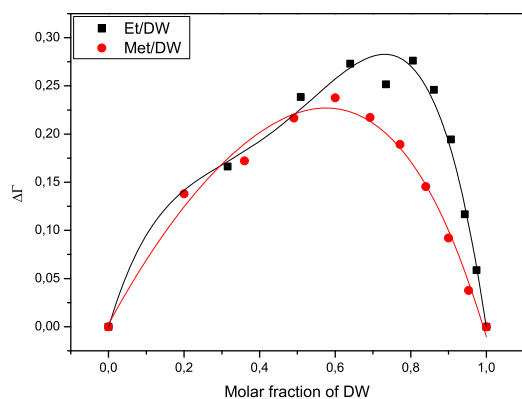


Fig. 8. Difference between the Grüneisen coefficient, vs. molar fraction of distilled water (DW), estimated with excess properties and the one estimated with additive ones.

$$\Delta\Gamma = \Gamma_{exc} - \Gamma_{ad}, \quad (7)$$

as shown in Fig. 8. It presents a maximum excess for higher molar fractions content of water.

Our results have some sources of uncertainty that can be improved. For instance, the use of very pure liquids, or by the use of smaller diameter pin-holes, in order to define better yet the position of the source of acoustic waves, finally, the use of a larger cuvette for the liquid might avoid possible influence of the shock-wave remnants in the signal and larger path to have more experimental points to fit. The main result here, is that all the difference between the speed of sound and its additive counterpart is due to the thermodynamic excess properties and that by the procedure presented here they can be visualized and analyzed quantitatively.

5. Conclusions

The speed of sound can be determined using the photoacoustic effect by means of simple measurements, namely the time-delay change of the beginning of the photoacoustic signal, related to the displacement of the laser with respect to the position of the PZT transducer.

Using this method we have determined the speed of sound in aqueous binary mixtures of liquids that undergo structural changes in solution that manifest as excess thermodynamic properties. These excesses produce changes in the speed of sound with respect to the composition, that do not obey the additive linear equation, especially near unity molar fraction of water in aqueous mixtures. The maximum of these discrepancies is very near the maximum of all the properties that depend on the specific volume of the mixture, namely the density, the compressibility, the isentropic heat capacity and the isothermal expansion coefficient, and the optical absorption coefficient.

Furthermore, we have presented the excess of the different thermodynamic properties that are of interest for the maximum of the photoacoustic signal. We have studied the excess in the absorption coefficient and compared it with other thermodynamic properties that present also the maximum excess at the nearly same molar fraction, for concentrations of water near the unity. The variation of the Grüneisen coefficient is presented here, the discrepancies with the additive one is crucial for understanding the photoacoustical signal generation.

We have also investigated the mixture ethyl-alcohol with methyl-alcohol, and shown that there is no noticeable difference

between the additive and the measured speed of sound, so we may infer that there is no structural change in their mixing.

This technique has the advantage of being straightforward both in data acquisition and in the interpretation, and as we have implemented it, it can be improved for more accurate measurements. It has also the advantage that the results are fast and readily obtained, which can be interesting in view of its possible applications to medical and biological studies.

We have summarized also the speed of sound measurements performed by other authors, in order to compare their results, which use much more involved systems, and ours, that do not differ appreciably.

Acknowledgements

D.I.I., J.A.P. and H.F.R.S. are members of the Carrera del Investigador Científico, Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET).

Authors acknowledge very useful discussions with Dr. Gabriel M. Bilmes.

This work was partially funded by Universidad Nacional del Centro de la Provincia de Buenos Aires (UNCPBA), by Agencia Nacional de Promoción Científica y Tecnológica (PICT 2008 No.70), and by CONICET (PIP 2010–2012 No.4).

References

- [1] Z. Xu, C. Li, L.V. Wang, Photoacoustic tomography of water in biological tissue, *Proc. SPIE* 7899 (2010) 789912.
- [2] Z. Xu, C. Li, L.V. Wang, Photoacoustic tomography of water in phantoms and tissue, *J. Biomed. Opt.* 15 (2010) 036019/1–036019/5.
- [3] A.C. Tam, Applications of photoacoustic sensing techniques, *Rev. Modern Phys.* 58 (1986) 381–431.
- [4] S. Manohar, A. Kharine, J. van Hespren, W. Steenbergen, S. van Leeuwen, Photoacoustic mammography laboratory prototype: imaging of breast tissue phantoms, *J. Biomed. Opt.* 9 (2004) 1172–1181.
- [5] M. Kinnunen, L. Myllylä, Effect of glucose on photoacoustic signals at the wavelengths of 1064 and 532 nm in pig blood and intralipid, *Appl. Phys.* 38 (2005) 2654–2661.
- [6] H. MacKenzie, H. Ashton, S. Spiers, Y. Shen, S. Freeborn, J. Hannigan, J. Lindberg, P. Rae, Advances in photoacoustic noninvasive glucose testing, *Clin. Chem.* 45 (1999) 1587–1595.
- [7] R. Dewhurst, T. Li, G. Gondek, Amplitude decay of photoacoustic signals in biological tissue when irradiated by nanosecond laser pulses, *Proc. SPIE* 6437 (2007) 643723/1–643723/12.
- [8] S. Boonsang, Photoacoustic generation mechanisms and measurement systems for biomedical applications, *Int. J. Appl. Biomed. Eng.* 2 (2009) 17–23.
- [9] L. Xi, X. Li, L. Yao, Design and evaluation of a hybrid photoacoustic tomography and diffuse optical tomography system for breast cancer detection, *Med. Phys.* 39 (2012) 2584–2594.
- [10] B. Wang, Q. Zhao, Photoacoustic tomography and fluorescence molecular tomography: a comparative study based on indocyanine green, *Med. Phys.* 39 (2012) 2512–2517.
- [11] G. Onori, Adiabatic compressibility and structure of aqueous solutions of ethyl-alcohol, *J. Chem. Phys.* 87 (1987) 1251–1255.
- [12] G. Onori, Adiabatic compressibility and structure of aqueous solutions of methyl-alcohol, *J. Chem. Phys.* 89 (1988) 4325–4332.
- [13] G. D'Arrigo, A. Paparelli, Sound propagation in water–ethanol mixtures at low temperatures. I. Ultrasonic velocity, *J. Chem. Phys.* 88 (1988) 405–415.
- [14] M. Mijakovic, B. Kezic, F. Sokolic, A. Asenbaum, C. Pruner, Ethanol–water mixtures: ultrasonics, Brillouin scattering and molecular dynamics, *J. Mol. Liq.* 164 (2011) 66–73.
- [15] G.C. Benson, O. Kiyohara, Thermodynamics of aqueous mixtures of non-electrolytes. I. Excess volume of water–n-alcohol mixtures at several temperatures, *J. Solut. Chem.* 9 (1980) 931–938.
- [16] G.C. Benson, O. Kiyohara, Thermodynamics of aqueous mixtures of non-electrolytes. II. Isobaric heat capacities of water–n-alcohol mixtures at 25 °C, *J. Solut. Chem.* 9 (1980) 791–804.
- [17] CRC Press, *Handbook of Chemistry and Physics*, 55 ed., 1974–1975, pp. D-203, D-211, F-11 and E-47.
- [18] J.A. Larkin, Thermodynamics properties of aqueous non-electrolyte mixtures I. Excess enthalpy for water + ethanol at 298.15 to 338.15 °K, *J. Chem. Thermodyn.* 7 (1975) 137–148.