ARCHIVES OF ACOUSTICS
31, 4 (Supplement), 143–152 (2006)

MOLECULAR ASSOCIATION AND RELAXATION PHENOMENA IN WATER SOLUTIONS OF ORGANIC LIQUIDS EXAMINED BY PHOTOACOUSTIC AND ULTRASONIC METHODS

B. B. J. LINDE, A. SIKORSKA, A. ŚLIWIŃSKI, W. ŻWIRBLA

University of Gdańsk
Institute of Experimental Physics
Wita Stwosza 57, 80-952 Gdańsk, Poland
e-mail: fizbl@univ.gda.pl

(*received June 15, 2006; accepted September 30, 2006*)

Examinations of water solutions of organic liquids carried out recently using both photoacoustic and ultrasonic methods have shown possibility of wider interpretation of the phenomena of clathrate structures creation (quasi stable associates) and relaxation processes taking place in water – glycols solutions. The discussion of the obtained results for mentioned above phenomena is presented. This allowed us for the comparison and common interpretation of the experimental results.

Key words: water solutions, molecular associates, photoacoustic and ultrasonic methods.

1. Introduction

Many experimental techniques have been developed in the last few decades to exploit photothermal [1, 6, 9, 18, 25] and ultrasound [19–21] propagation effects for examination of liquid media. We have shown that, application concurrently the both methods [31–34] gives possibility of more complete interpretation of molecular phenomena taking place in such media.

In the paper we shall give some examples of using both measuring methods (photoacoustic and ultrasonic ones) for examination of water solutions of organic liquids and a discussion of the obtained experimental results in the light of association mechanisms in such media. The concentration dependent changes of two thermal parameters: diffusivity and effusivity will be presented and compared with the changes of elastic parameter: adiabatic compressibility for water solutions of some polymers.

2. Application of photoacoustic spectroscopy (PAS) for examination of water solutions

Photoacoustic measuring methods based on the theory developed by Rosencwaig [28, 29] were recently successfully applied for examinations of various solid and liquid media [2, 6, 9, 15–17]. Photoacoustic spectroscopy (PAS), commonly used in the case of solids, as applied to liquids is essentially based on the same phenomenon, however technical apparatus details, particularly measuring cell and mode of registration require a proper adaptation.

In investigations of water solutions PAS is used to determine various thermo physical and structural characteristics. Due to the development of phototermal techniques in last years accurate determination of thermal characteristics became possible, e.g. such as thermal effusivity (1) and diffusivity (2) or thermal conductivity coefficient dependence on the solution concentration. Here:

$$e = \sqrt{\rho c_p k}, \tag{1}$$

$$\alpha = \frac{k}{\rho\, c_p}. \tag{2}$$

where ρ – density, c_p – specific heat, k – thermal conductivity.

Especially useful techniques for that purpose are the microphone photoacoustic (PA) and the photopyroelectric (PPE) ones. In the case of liquids a quantitative interpretation of photoacoustic measurements using a closed PA cell become complicated because of other contributions to a total signal coming from periodic evaporation and condensation of a liquid or its periodic expansion. The effects can substantially change the pressure in the cell in respect to the acoustic pressure due to the pure photothermal phenomenon. The difficulties can be avoided using so called open cell technique. The idea of the experiment using such PA cell was presented in the papers [23, 27]. The configuration of an experiment is schematically shown in Fig. 1.

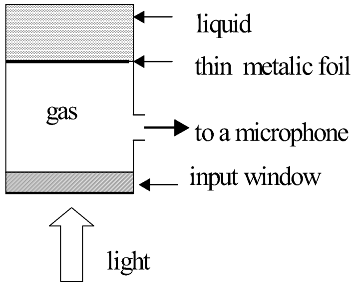

Fig. 1. The idea of photoacoustic measurement using the open PA cell. The photoacoustic signal is generated due to absorption of light by the metal foil. The heat created in the foil is transmitted to the liquid placed behind it. Thus the value of PA signal depends on thermal properties of the liquid.

PAS measurements for this paper were performed in the cell above in PA arrangement described in [31].

3. Application of the ultrasonic spectroscopy (US) for examination of water solutions

The ultrasonic spectroscopy is one of many methods permitting to examine molecular structures created in water solutions, particularly in polymer ones. To understand the conception of “water structures” or the definition of “hydrogen bonds” it is important to explain what is the role of water itself in such solutions. To do that one can create a model of molecular interactions in water solutions of polymers. The hydrogen bonds are a base of understanding of properties of water and its solutions. The hydrogen bond determines a specific interaction between an electronegative atom (e.g.: N, O, F or Cl) and a hydrogen atom or its heavy equivalent deuteron. Particularly then, when it is directly chemically connected with an electronegative atom [26, 35]. Hydrogen bonds are strongly directional what means that chemical bond containing a donor of hydrogen bond, hydrogen or deuteron, tends to take such a direction in order to indicate position of the electronegative atom being an acceptor of that bonding. The interaction energy of typical hydrogen bond (~ 20 kJ/mol) is an intermediate value between the energy of the weak interaction of the Van der Waals type (~ 2 kJ/mol) and the energy typical for chemical bonds (~ 400 kJ/mol).

The creation of water structures (associates) with a participation of a hydrophobic substance or of a hydrophobic part of molecules dissolved in water has been already suggested in forties [13], however creation of hydrates was found rather later [14]. Hydrates which are created due to the saturation of water by gasses or by mixture of gases appear as non-stoichiometric structures. Such stabilising effect is described using a “guest-host” model. The organic molecule is situated in a cavity created in the construction skeleton of water (clathrate structure). The cavity in pure water is occupied, at least partially by monomeric water molecules [8, 36].

Many of organic compounds create a clathrate structure in solid state interacting with the water structure which plays a role of the “host”. The presence of a molecule of the “guest” stabilises the clathrate structure. In this way we also try to explain interesting properties of binary mixtures of non-electrolites and water. The quasi crystalline lattice of water non-stabilised by the “guest” is metastable, it cannot last permanently, so it differs from the crystallic lattice of the ice. Creation of these clathrate structures is possible in the case of small “guest” molecules e.g. of dioxane [20]. For molecules of sizes larger than the cavity dimensions appearing in the water lattice the situation is a little different.

3.1. Interaction mechanism of ultrasonic wave and molecular structure in binary mixtures of water and organic compounds

The molecular structure of a medium has an essential influence on its elastic properties, which determine propagation conditions of ultrasonic waves and their velocity values directly measured and together with density used to characterise the medium. In liquids then, when dispersion could be neglected, the results of measurements of sound velocity and density can be expressed by the coefficient of adiabatic compressibility using (3) Laplace formula

$$\beta_{\mathrm{ad}} = \frac{1}{\rho\, c^2}\,, \tag{3}$$

where ρ is density and c velocity of sound in liquids examined.

Results of isothermic measurements in water solutions of organic compounds (non-electrolites) show that on the plots of the adiabatic compressibility coefficient versus the molar fraction of the solute, there appear two characteristic points in the range of low values of concentration i.e. crossing of the isotherms and their minimum. These regularities appear due to structural interactions which are attributed to creation of clathrate-like structures of type I and II. BAUMGARTNER and ATKINSON [3] attribute creation of such structures to the point of minimum of the adiabatic compressibility coefficient while according to ENDO [12] such packing structure appears for the concentration corresponding to the crossing of the isotherms. Acoustical investigations performed for polyethylene glycols 1000 and 1540 showed similar behaviour however it was found that these substances were not able to form the clathrates of type I or II [30].

Polyethylene glycol (PEG) examined by us presents a simple molecular structure $OH\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$ and it is very good object to look for structural effects because of existing of hydrogen as well as etheric bonds which can create hydrogen bridges with water molecules. Another advantage of this polymer while examining hydration of molecules is the dependence of its properties on temperature and concentration of its water solutions. However the most interesting is the fact that PEG can appear in the form of helix [5]. In such configuration of molecules the distance between two adjacent oxygen atoms (along the total chain of the molecule) is very close (0.88 Å) to the length of O-O bond in liquid water (2.85 Å) [7].

In the paper a model of molecular interaction in systems of polyethylene glycols 200 and 400 as well as ethylene glycol has been proposed on the basis of acoustical investigation results taking into account phenomena of hydration and appearing of hydrogen bridges.

3.2. Application of ultrasonic spectroscopy (US) in examination of association processes in water solutions

3.2.1. Experimental

Measurements of sound velocity of water mixtures of ethylene glycol (EG), polyethylene glycols (PEG) 200, 400 were performed in the temperature range from 291.15 to 303.15 K using ultrasonic waves velocity meter MPFU. The measurements based on the determination of an averaged time of passing through the sample by an acoustic signal with frequencies between 1 and 10 MHz. The method is similar to the sing-around technique and with the same accuracy. The instrument was calibrated by measuring the velocity in standard liquids. The velocity was measured with an accuracy better than $\pm 0.02\%$. The density was measured with the density meter type MG-2P, ECOLAB calibrated with the known values for water and air.

3.2.2. Measurement results

In Fig. 2 the results of experimental examinations of the adiabatic compressibility versus the molar fraction for water solutions of PEG 200 are presented. The plot describes variation of the compressibility coefficient for different temperatures. The two characteristic points mentioned above (crossing of isotherms and their minimum) are visible, too. The measurement results obtained for EG proved to be, however, substantially different. Though the isotherms crossed in one point but there was difficult to determine undoubtedly the minimum for such system (Fig. 3).

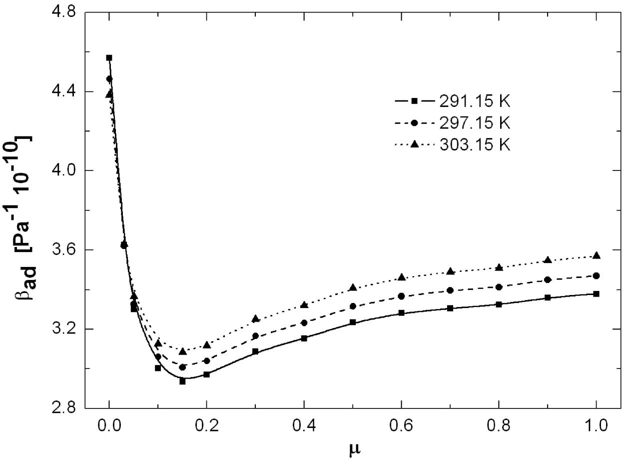

Fig. 2. PEG 200/water adiabatic compressibility isotherms for the total mole fraction in the temperature range from 291.15 to 303.15 K.

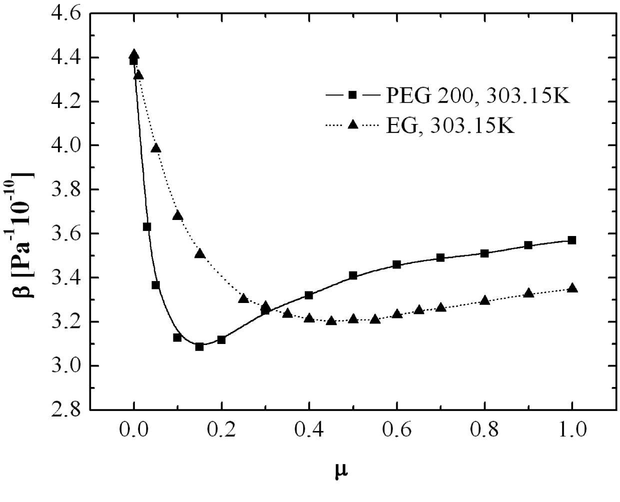

Fig. 3. Adiabatic compressibility isotherms for the system: EG, PEG 200 at 303.15 K.

The adiabatic compressibility coefficient for the PEG solution reaches its minimum value at the mole concentration about 0.14. Using the results one can calculate how many molecules of water is bonded by one molecule of PEG at this concentration. Polyethylene glycol 200 had the minimum of compressibility coefficient by the ratio of the polymer to water equal to $1 : 6.1$. These results can be explained basing on a following model : addition of water to the polymer effects creation of hydrogen bonds between water and oxygen atoms of etheric bond. Basically, each oxygen atom from the etheric group can be an acceptor of two hydrogen bonds. Moreover, at the end of each molecule of the polymer also oxygen atoms are situated.

Some papers based on infrared spectra measurements [5] and diffraction of neutrons [4] suggested few possible hydrogen bonds in similar molecular systems. One of the models has assumed that two adjacent oxygen atoms of etheric groups are able to bond one molecule of water. Taking into account such position of hydrogen bridges allowed us to calculate amount of water needed for obtaining the first hydration shell. The number of water molecules associated with PEG 200 proved to be equal to 6. Such amount of water is close to the concentration of PEG 200 water solutions for which the minimum of compressibility was observed. The characteristic minimum is not observed for the system of ethylene glycol and water. It might be due to a lack of etheric bonds in examined system which are able to stiffen the associates in the case of polyglicols and water.

Increasing the amount of water in the solution besides the minimum of the compressibility one can also observed the crossing point of isotherms. That point then determines the concentration at which a change of the temperature, in a narrow range of concentration, does not influence the stability of the structure. The adiabatic compressibility coefficient corresponding to the crossing point of the isotherms appears for the concentration of circa 0.116 for EG solution and 0.031 for PEG 200. At those points for which $\mathrm{d}\beta_{\mathrm{ad}}/\mathrm{d}T \approx 0$, the stoichiometric ratio of ethylene glycol to water is equal to $1 : 7.6$; however $1 : 31$ for polyethylene glycol 200. So, a question arises what is the phenomenon we are dealing with.

It was found from neutron diffraction investigations [7] of long chain polymers of PEG (called PEO) that in hydration process of these substances two ranges of the hydration can be determined. Also, there was given a presumable stoichiometry for hydration process, namely it was found that on every monomer of PEO fell 6 molecules of water. Taking into account that information one can calculate the stoichiometry of such system. The results are following: for PEG 200 the number of water molecules needed to above mentioned interactions is equal to 26, for PEG 400 it is the number 56, however for EG it is the number 6. From results of ultrasonic investigations in binary mixtures one can draw out similar conclusions as from results described in the already mentioned papers [7].

4. Examples of examination results of water solutions of organic liquids using both PAS and SU methods

In the PAS literature one can find theoretical considerations on a possibility of measurements of thermal parameters of liquids using the PAS open cell described above. Also absolute values of effusivity and diffusivity for some pure liquids obtained applying such cell are available [2, 11, 22]. Taking advantage of resonance cavity for thermal waves and increased sensibility of signal processing, so called “common mode rejection” were applied to detection of trace amounts of methanol in water [24]. Recently, attempts were undertaken to apply the photothermal techniques for evidencing molecular association processes in binary mixtures of liquids by investigation concentration changes of thermal parameters of those mixtures. In paper [10] a theoretical model was presented based on applying the linear superposition principle for some thermal parameters of a liquid mixture. It assumes, that the new medium arising due to interaction between components of liquid mixture containing complexes of the components will differ in thermal parameters from the input liquids. At a large enough concentration of the solute in the mixture there occurs a lack of the solvent molecules to continue the association process. According to the model attaining of such concentration corresponds to the maximal deviation from the linear dependence between values of the parameter and the mass concentration of the solute.

5. Comparison of PAS and US results, their discussion and interpretation

As mentioned in Sec. 3, basing on analysis of the compressibility of a liquid mixture versus the mole concentration one can deduce about the interaction between mixture components. To verify and complete the information one can use a parallel measurement of different physical quantity characterising the examined mixtures e.g. effusivity or diffusivity by PAS method.

Experimental verification of successful application of the proposed model to a selected coefficient characterising a solution requires determination of variations of thermal parameters for different concentrations with very good precision. Application of the open PAS cell with the photoacoustic microphone (PAM) detection to measure the thermal effusivity of water mixtures of ethylene alcohol has been presented in [32]. Results of examinations of thermal diffusivity versus the concentration of some water solutions using the photothermal technique with photopyroelectric signal detection are given in papers [10, 25] and in [18] the thermal waves interferometer was applied.

Examples of examination results performed in parallel using both PAS and US methods in water solutions of ethylene glycol, EG, and in compounds belonging to the homologous series of polyethylene glycols with various molecular mass: DEG, PEG 200 and PEG 400 were presented in paper [34]. Basing on photoacoustic and photopyroelectric measurements a deviation from linear behaviour versus the weight concentration was found for effusivity as well as for diffusivity in water solutions of PEG 200 and PEG 400 (see an example presented in Fig. 4). However, for mixtures of EG with DEG the linear dependence of effusivity against the mass concentration was found with 1% precision what confirmed the assumption of applicability of the linear superposition rule to this quantity in the lack of interaction between the components of the solution.

Simultaneously, examinations of the adiabatic compressibility coefficient variation against the concentration for the same solutions were performed. As shown in Fig. 2 the adiabatic compressibility coefficient for the PEG 200 solution have the minimum for the mole concentration circa 0.14 what corresponds to circa 0.65 of mass concentration.

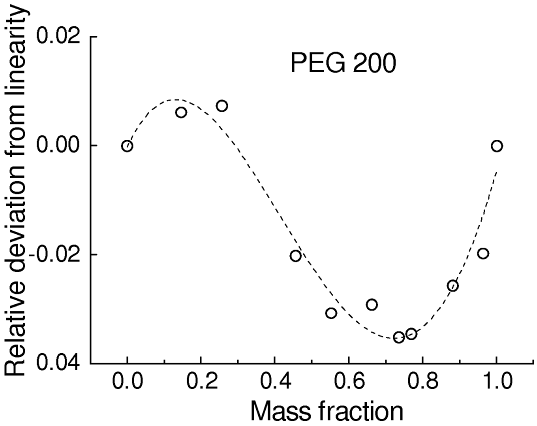

Fig. 4. Relative deviation of thermal effusivity from linearity versus weight concentration of PEG 200 in water solution. For the value of circa 0.7 of the concentration the curve attains minimum.

For the mixture of two liquids (EG and DEG) which due to their structure should not interact through hydrogen bonds the characteristic for the compressibility obtained was with a great precision a linear function of mole concentration.

As it results from the comparison of Fig. 2 and Fig. 4 the range of concentration for which appears the largest deviation from linearity of both thermal characteristics reasonably covers the range of minimal values of compressibility coefficient. Therefore, one can assume that the observed variations of thermal parameters and the elastic quantities in water solutions reflect the same interaction mechanism, in this case creation of the hydration zone around the molecule of the dissolved polymer.

6. Conclusions

The above discussion supported by the obtained measuring results permits to formulate the following thesis:

- addition of a polymer to water causes creation of the characteristic point of a minimum in the plot of adiabatic compressibility coefficient dependence versus the concentration resulting from the creation of the first hydration zone around the molecule of a polymer;
- concentration characteristics of thermal parameters obtained for water solutions of PEG 200 from photothermal measurements show towards creation of associates in the same range of concentration for which appears the minimum of the adiabatic compressibility coefficient;
- for ethylene glycol the location of shallow minimum is difficult to determine with high precision. This can be attributed to the lack of strong enough molecular interaction for creation of a “stiff” hydrated complex;
- as a result of addition of water the hydrated polymer molecules “swell”, the compressibility coefficient increases and the system becomes more elastic;

- the crossing point of isotherms of the compressibility corresponds to the second hydration zone;
- based on the similarity between distances of the consecutive oxygen atoms in the polymer molecule and in liquid water and the results of the paper [37] one can to identify molecules which really stiffen the system examined. Taking into account the results obtained for solutions of ethylene glycol and polyethylene glycols one can conclude that the later caused stabilisation of the system.

Acknowledgments

The work was supported by the Polish Ministry of Science and Higher Education grant No. 4T07 B024 29 and performed in 2005–2008.

References

[1] ALMOND D. P., PATEL P. M., *Photothermal science and techniques*, Chapman &Hall, London 1996.

[2] BALDERAS-LOPEZ A., GUTIERREZ-JUAREZ G., FONASECAAND M., SANCHEZ–SINENCIO F., Rev. Sci. Instrum., **70**, 2069 (1999).

[3] BAUMGARTNER E. K., ATKINSON G., J. Phys. Chem., **75**, 2336 (1971).

[4] BARNES A. C., BIEZE T. W. N., ENDERBY J. E., LEYTE J. C., J. Phys. Chem., **98**, 1527 (1994).

[5] BEGUM R., MATSUURA H., J. Chem. Soc., Faraday Trans., **93**, 21, 3839 (1997).

[6] BENTEFOUR E. H., GLORIEUX C., *et al.* , J. Appl. Phys., **93**, 9610–9614 (2003).

[7] BIEZE T. W. N., BARNES A. C., HUIGE C. J. M., ENDERBY J. E., LEYTE J. C., J. Phys. Chem., **98**, 6568 (1994).

[8] BUSLAEVA M. N., SAMOILOV O. YA., Zhur. Strukt. Khim., **4**, 502 (1963).

[9] CAERELS J., GLORIEUX C., THOEN J., Rev. Sci. Instr., **69**, 2452–2458 (2003).

[10] DADARLAT D., CHIRTOC M., NEMATU C., CANDEA R., BICANIC D., Phys. Status Solidi, **K121, K23** (1990).

[11] DELGADO–VASALLO O., VALDES A., MARIN E., LIMA J. A., DA SILVA M. G., STHEL M., VARGAS H., CARDOSO S., Meas. Sci. Technol., **11**, 412–417 (2000).

[12] ENDO H., Bull. Chem. Soc. Jpn., **46**, 1106 (1973).

[13] FRANK, EVANS M. W., J. Chem. Phys., **13**, 507 (1945).

[14] FROST F., DEATON M. N., *Gas hydrates and their relation to the operation of natural gas pipe lines*, Bur. Mines, New York 1946.

[15] GUTIERREZ–JUAREZ G., *et al.* , Rev. Sci. Instr., **74**, 845 (2003).

[16] KAWSKI A., *Fotoluminescencja roztworów*, Ch. 8, 137–143, PWN, Warszawa 1992.

[17] LANDA A., *et al.* , Rev. Sci. Instr., **74**, 377 (2003).

[18] LIMA J., MARIN E., MASUNGA M., CORREA O., CARDOSO S., VARGAS H., MIRANDA L., Appl. Phys., **B 73**, 151–155 (2000).

[19] LINDE B. B. J., *Acoustical spectroscopy of cyclic and heterocyclic compounds, ketons and polluted water surface*, Wyd. Uniwersytetu Gdańskiego, 1–243, 1997.

[20] LINDE B. B. J., ROSENFELD E., CHRIST A., Mol. Quant. Acoust., **19**, 149–158 (1999).

[21] LINDE B. B. J., SOROKA J., BORKOWSKI M., Forschrite der Akustik, DAGA'02, Bochum, 708–709 (2002).

[22] MALIŃSKI M., *et al.* , Proc. 4-th Workshop on Photoacoust & Phototherm., 129 (1999).

[23] MARQUEZINI M., CELLA N., MANSANARES A., VARGAS H., Meas. Sci. Technol., **2**, 396–401 (1991).

[24] MATVIENKO A., MANDELIS A., J. Phys. IV France, **125**, 269–271 (2005).

[25] NEAMTU C., DADARLAT D., CHIRTOC M., HADJ SAHRAOUI A., LONGUEMART S., BICANIC D., Instr. Sci. Technol., **34**, 225 (2006).

[26] PAULING L., *The nature of the chemical bond*, Oxford Univ. Press, 1945.

[27] PERONDI L. F., MIRANDA L. C. M., J. Appl. Phys., **62**, 2955–2959 (1987).

[28] ROSENCWAIG A., GERSHO A., J. Appl. Phys., **47**, 64 (1976).

[29] ROSENCWAIG A., *Photoacoustics and photoacoustic spectroscopy*, Wiley, New York 1980.

[30] SCHMELZER C. E. H., ŻWIRBLA W., ROSENFELD E., LINDE B. B. J., J. Mol. Struct., **699**, 47 (2004).

[31] SIKORSKA A., LINDE B. B. J., Journ. de Phys. IV, **109**, 99–104 (2003).

[32] SIKORSKA A., LINDE B. B. J., Journ. de Phys. IV, **117**, 73–78 (2004).

[33] SIKORSKA A., LINDE B. B. J., ŻWIRBLA W., Chem. Phys., **31**, 320 (2005).

[34] SIKORSKA A., DADARLAT D., LINDE B., STREZA M., NEAMTU C., ŚLIWIŃSKI A., J. Phys., IV (2006) (in print).

[35] VINOGRADOV S. N, LINNEL R., *Hydrogen bonding*, van Nostyrand Reinhold, New York 1971.

[36] YASHKITSHEV V. N., SAMOILOV O. YA., Zhur. Strukt. Khim., **3**, 211 (1962).

[37] ŻWIRBLA W., SIKORSKA A., LINDE B. B. J., J. Mol. Structure, **743**, 49 (2005).