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Photoacoustic Method as a Tool for Analysis of Concentration-Dependent Thermal Effusivity in a Mixture of Methyl Alcohol and Water

Nikodem PONIKWICKI(1), Łukasz SZCZEPANIK(1), Joanna GONDEK(1)
Bogumił B.J. LINDE(1), Ewa Barbara SKRODZKA(2)*, Vladimir MOLCHANOV(3)
Konstantin B. YUSHKOV(3), Rostislav GRECHISHKIN(4)

(1) *Institute of Experimental Physics*
University of Gdansk
Gdańsk, Poland

(2) *Institute of Acoustics, Faculty of Physics*
A. Mickiewicz University
Umultowska 85, 61-612 Poznań, Poland
*Corresponding Author e-mail: afa@amu.edu.pl

(3) *National University of Science and Technology "MISIS"*
119049 Moscow, Russia

(4) *Department of Physics, Tver State University*
170100 Tver, Russia

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It has been shown in the present paper that exploitation of the experimental potential of a photoacoustic technique can provide information on a type of intermolecular interactions in aqueous mixtures containing organic liquids, when the basic parameters of these mixtures, such as density, ρ, specific heat, c_p, or thermal conductivity, λ, are unknown. Earlier investigations of concentration dependence of effusivity in different aqueous solutions of organic liquids demonstrated that the photoacoustics method is a sensitive tool to identify hydrophobic properties of such liquids. In our experiment this suggestion was exploited for a solution of methanol which is known to display much weaker hydrophobicity than other alcohols.

It was confirmed that the location of extreme deviations from linearity for the thermal effusivity, Δe, agrees well with that of characteristic points for the isentropic compressibility coefficient, κ_S, and the excess molar volume, V_m^E, as a function of the concentration.

Keywords: thermal effusivity; aqueous solutions; methanol; photoacoustic technique.

1. Introduction

1.1. Characteristic features of solutions of nonpolar liquids and problems with their interpretation

Aqueous solutions of organic liquids can be encountered practically everywhere. Their properties have been objects of interest in science and technology for a long time in both cognitive and practical aspects (Sikorska, Linde, 2008). Among them, aqueous mixtures of liquids containing nonpolar molecular groups which do not react chemically with water, occupy a special position. When mixed with water, they display the so-called hydrophobic effect. Unlike solutions of "ordinary" (polar) liquids, the solutions of hydrophobic liquids at low concentrations exhibit a high negative excess molar volume and isothermal compressibility and positive values of certain excess thermodynamic functions (Turgut *et al.*, 2008; Franks, 2000) (Table 1).

Interest of researchers has been focussed for years on high deficiency of entropy in the mixing process of nonpolar liquids and water while compared to that characteristic for the so-called ideal solution. Until re-

Table 1. Limiting thermodynamic excess functions of hydrophobic and "normal" solutes in aqueous solutions ($\Delta X^E = \Delta X_{\text{exp}} - \Delta X_{id}$) after Franks (2000).

Function	Hydrophobic solutes	Polar (normal) solutes
Free energy	+	–
Enthalpy	+ or –	–
Entropy	– $\text{abs}(T\Delta S) > \text{abs}(\Delta H)$	– $\text{abs}(T\Delta S) < \text{abs}(\Delta H)$
Heat capacity	+	–
Volume	–	small
Compressibility	– (small)	–

cently, this phenomenon, confirmed by numerous observations, has been commonly associated with the iceberg theory (Frank, Evans, 1945), according to which water's structure in the vicinity of a nonpolar molecule is strengthened and braced. As a result, structures analogous to solid clathrate compounds are formed (Shi *et al.*, 1992). The accompanying reduction in degrees of freedom of water in the neighbourhood of a nonpolar molecule could be the reason of a too small increase in the mixture's entropy.

When molecules of a liquid mixed with water contain both nonpolar and polar groups, such mixture can exhibit features of the two competing effects: hydrophobic and hydrophilic. Monohydric alcohols containing nonpolar, CH_3 and CH_2, and polar OH groups are typical examples of such liquids. Physical properties of their aqueous solutions belong to relatively well, if not best, recognized and described. Nonetheless, the discussion on interpretation of the phenomena accompanying the dissolving process in such solutions has not been closed yet.

In the past decade there has been a rapid development in experimental techniques on the molecular level, such as time-dependent X-ray and NMR spectroscopy or analysis of diffraction distribution of X-rays and neutrons. The advancement in measurement methods was concomitant with a brisk development of computer techniques and methods of data processing. As a result, not only new data have been obtained but new suggestions for their theoretical interpretation have been formulated (Soper *et al.*, 2006; Dixit *et al.*, 2002; Sato, Buchner, 2005). However, the ultimate verification of the theory is in consistence with the observed macroscopic properties of the medium examined. In practice, even in the case of relatively exhaustively examined water solutions of alcohols, the literature data on quantities such as density, ρ, thermal conductivity, λ, or specific heat, c_p, of solutions are either incomplete or not easily accessible.

The aim of the paper is to show that the results provided by the simple photoacoustic method (PA) used to measure effusivity are comparable to the ones delivered by other techniques, such as ultrasonic, dielectric, mass or IR spectrometry.

1.2. Contemporary views on mixing processes in water solutions of methanol

The simplest alcohol soluble in water, methanol, is a good conductor and is used as a component of cooling mixtures. Except for the OH group it contains only the CH_3 group and is devoid of the CH_2 group. Seemingly, it is well soluble in water and, owing to the OH group, it provides both acceptors and donors of hydrogen bonds. In reality, when mixed with water, methanol causes the formation of a dynamic mixture of methanol associates, water and water-methanol. This means that on the microscopic level the composition of the solution is inhomogeneous and the solubility is incomplete. On the basis of analysis of the diffraction pattern of neutrons diffracted by water-methanol mixtures of various concentrations (Soper *et al.*, 2006), a hypothesis has been formulated that the anomalously low increase of the mixing entropy of methanol-water solution corresponds quantitatively to a model based only on experimentally observed micromolecular segregation of components. A simple theoretical explanation of this phenomenon was given which does not require employment of the idea of water restructuring (Dixit *et al.*, 2002). The authors suggest that micro-clusters formed in the mixture and their bi-percolations suffice enough to ensure a negative contribution to the entropy of mixing.

It has been suggested in the last decade (Sato, Buchner, 2005) that the role of the nonpolar alcohol group is to protect the OH group against contacts with free water (i.e. water not bound in a quasi-lattice structure). Owing to the presence of nonpolar groups the lifetime of the so-called free water lengthens, which means slowing down of the dynamic reorganization of the whole water lattice with built-in alcohol OH groups. It is supposed that the OH groups present a steric hindrance, causing a local drop in the number of acceptors and donors of hydrogen bonds between the OH groups of methanol and free water when compared with the situation in pure water. As a result, the mean strength of hydrogen bonds in the solution changes which is followed by a change in enthalpy of the solution. The observed maxima of the excess enthalpy of activation of the dielectric relaxation collective component in three monohydric alcohol solutions correspond to similar values of the alcohol mass fractions (Sato, Buchner, 2005).

Concentration dependences of thermodynamic quantities of this mixture with methanol are usually untypical when compared to those obtained for other monohydric alcohols. The excess molar heat capacity can be considered one of the examples. Although it exhibits at high dilutions a maximum typical for hydrophobic compounds yet this maximum appears not only to be weaker but also corresponds to higher molar concentrations than in case of similar maxima characteristic for a homologous series of alcohols (Benson *et al.*, 1980). The partial molar volume of methanol in a water solution has a minimum at a much higher methanol concentration than in case of ethanol and other alcohols from the series (Franks, 2000). This minimum is also shallower than those typical for other alcohols (Franks, 2000), while the partial molar volume of water in such solution shows an untypically high maximum in the region of low methanol concentrations (Marcus, 2011).

The investigation of the dependence of effusivity, a macroscopic thermal parameter, on methanol concentration allows comparisons with relevant dependences obtained earlier for other alcohols (Sikorska *et al.*, 2010).

2. Measurement methods

2.1. Determination of thermal effusivity of liquids by the photoacoustic method

As demonstrated earlier (Sikorska, Linde, 2008; Franks, 2000; Balderas-Lopez *et al.*, 1999), measurement of amplitude or phase of photoacoustic signal delivered by a sample consisting of light absorbing metal foil and a layer of liquid placed on the foil allows determination of the liquid's effusivity:

$$e = \sqrt{\rho \cdot \lambda \cdot c_p}. \tag{1}$$

This parameter is defined as the square root of the product of three quantities describing the properties of a material: ρ – the density, λ – the thermal conductivity and c_p – specific heat of the sample.

An open photoacoustic chamber used in our experiment (Sikorska, Linde, 2008) operated in front configuration. A thermally thick layer of the investigated liquid was placed on a thin metal foil closing the chamber from the above. The foil served also as an absorber responsible for generation of photoacoustic signal. The chamber was equipped with a transparent window through which the sample-foil system was illuminated with a frequency-modulated laser light. Thermal effusivity of the liquid was determined by measuring the photoacoustic signal amplitude which was dependent on the properties of the liquid placed on the foil (Sikorska, Linde, 2008). The intensity of the laser light monitored by means of a Si optical power probe was constant in time and its fluctuations did not exceed 1% per hour.

The detailed description of our experiments aimed at determination of effusivity and the results of the first measurements are presented in another paper (Sikorska, Linde, 2003). The idea of an open-cell method is illustrated in Fig. 1. Thermally thick layer of liquid under investigation was placed on a thin metal foil, which closed the PA cell from the top. In our experiment the foil was 60 μm thick, aluminium absorber. It was illuminated by modulated, expanded beam of light, coming from a diode laser light (15 mW output power, 1 cm diameter), through a transparent entrance window of the cell. Teflon ring and the foil bottom formed a tight container into which the investigated liquid was poured. The pressure signal generated in air gas filling the PA cell was registered by a microphone and stored by a computer. The obtained PA signal amplitudes were analysed based on the one dimensional Rosencwaig-Gersho (1976) theory.

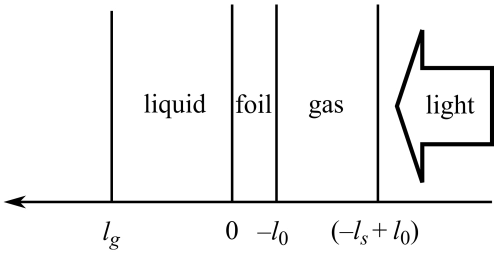

Fig. 1. The experimental configuration applied for effusivity determination, from (Sikorska, Linde, 2003).

The following conditions were rigorously kept at the experimental procedure: liquid samples were thermally thick, i.e. $l_s > \mu_s$ in the whole range of the used modulation frequencies. Here: l_s is the liquid column thickness, $\mu_s = \sqrt{\frac{\alpha_s}{\pi f}}$ denotes thermal diffusion way, α_s is thermal diffusivity of the liquid sample, and f represents light modulation frequency. In our experiment l_s is equalled 0.2 cm. The values of thermal parameters that we used for calculations are collected in Table 2.

Table 2. Thermal parameters of the materials used in the experiment.

	α [cm^2/s]	μ [cm] for f = 100 Hz	e [W·s$^{0.5}$/(K·cm^2)]
Aluminium	0.98[a]	0.03[a]	2.4[a]
Water	$1.14 \cdot 10^{-3}$ [b]	0.019[a]	0.16[a]
Ethyl alcohol	$8.9 \cdot 10^{-4}$ [c]	0.0017[c]	0.06[c]

[a] (Favro *et al.*, 1987)
[b] (Hartikainen *et al.*, 1991)
[c] (Rosencwaig, 1988).

The examined liquid was in a good thermal contact with a metal foil reference, which was thermally thin, $\mu_r > l_r$, but optically very thick (opaque), i.e. $\beta_r \mu_r \gg l_r$ (μ_r is thermal diffusion length and β_r light absorption coefficient of the reference material) (Sikorska *et al.*, 2005). The modulation frequency, f, was restricted by the condition $f \ll f_c = \alpha_r / \pi l_r^2$.

Under these experimental conditions it seems quite reasonable to assume that any additional mechanical contributions to the measured PA signal do not seriously affect the PA amplitudes ratio. The maximum error of the PA signal amplitude measurement (determined for distilled water placed on the foil) did not exceed ±1%.

3. Experimental results and discussion

3.1. *Thermal effusivity dependence of methanol-water mixture on methanol concentration*

Changes in effusivity which is an intensive macroscopic parameter, were investigated as a function of mass fraction, w_1, of the solute. To validate concentration dependence of effusivity determined by the photoacoustic method (Eq. (1)), we used relevant densities measured by our group, the data referring to specific heat obtained by (Benson *et al.*, 1980) and that of thermal conductivity published by other authors (Assael *et al.*, 1989; Pandey *et al.*, 2005).

As shown in Fig. 2, the effusivity dependence on the mass fraction of methanol is close to linear. A more detailed analysis revealing actual deviation of effusivity from a straight line will be shown in Subsec. 3.3.

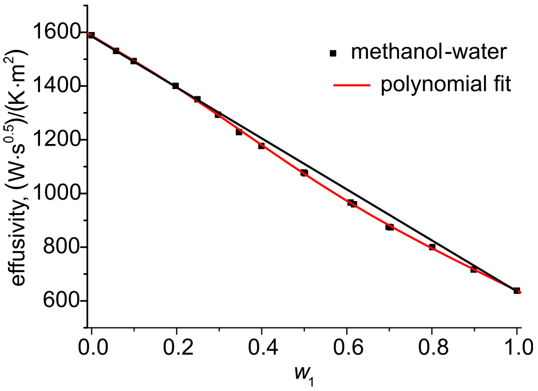

Fig. 2. Dependence of thermal effusivity, e, of aqueous methanol solution on the mass fraction w_1 of methanol at T = 25°C, obtained by the photoacoustic method.

3.2. *Verification of the measurement procedure of the methanol-water mixture effusivity. Determination of thermal conductivity*

In order to verify our measurements, first the experimental data shown in Fig. 2 were used to calculate corresponding thermal conductivity values (Sikorska, Linde, 2008; Sikorska *et al.*, 2010; Almond, Patel, 1996). The required densities of solutions were determined by means of an Anton Paar liquid density meter while relevant specific heat values were calculated using the presented in Fig. 3 data of excess specific heat published by Benson *et al.* (1980).

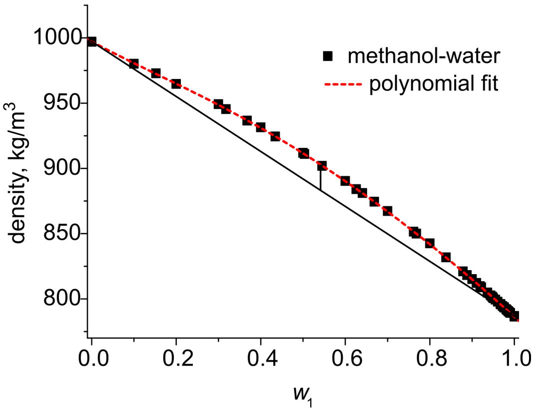

Fig. 3. Dependence of the density of aqueous methanol solution on the mass fraction w_1 of methanol at T = 25°C.

Then, the obtained dependence of thermal conductivity on the mass fraction of methanol was compared with the literature data (Assael *et al.*, 1989) and also with the values calculated using the semi-empirical formula given in (Pandey, Mishra, 2005):

$$\lambda_{\text{mix}} = \frac{\lambda_1}{1 + A_{12}\left(\frac{x_2}{x_1}\right)} + \frac{\lambda_2}{1 + A_{21}\left(\frac{x_1}{x_2}\right)}, \tag{2}$$

where λ_1 and λ_2 are thermal conductivities of pure liquid 1 and 2, correspondingly.

Coefficients A_{ij} express the efficiencies with which molecules 1 and 2 counteract the momentum transport

$$A_{12} = \frac{1}{4}\left[1 + \left(\frac{\lambda_1}{\lambda_2}\right)^{1/2}\left(\frac{M_2}{M_1}\right)^{3/8}\right]^2, \tag{3}$$

where M_1 and M_2 – molar masses of liquid 1 and 2, respectively.

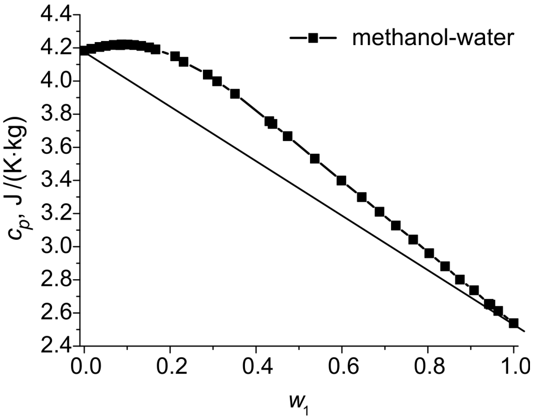

Fig. 4. Dependence of specific heat of aqueous methanol solution on the mass fraction w_1 of methanol at T = 25°C.

Graphical comparison of concentration dependence of thermal conductivities determined by all the discussed above methods is shown in Fig. 5. As can be seen the data calculated using the experimental results obtained for thermal effusivity (from PA measurements) are in a good agreement with both the measurement data given in (Assael, 1989) and the values calculated from the semi-empirical formula presented in (Pandey, Mishra, 2005).

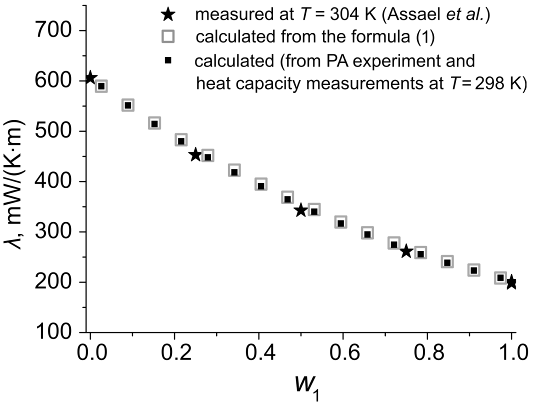

Fig. 5. Dependence of thermal conductivity of the methanol-water mixture on the mass fraction w_1 of methanol.

3.3. Comparison of concentration-dependent changes in effusivity for aqueous solutions of different monohydric alcohols

To analyse precisely the concentration dependence of effusivity, first the deviation from linearity was determined for each type of mixture and next obtained values were divided by effusivity of water, e = 1589 $(\mathrm{W}\cdot\mathrm{s}^{0.5})/(\mathrm{K}\cdot\mathrm{m}^2)$. According to our previous findings (Sikorska, Linde, 2008), one may regard this deviation as a result of the interactions between the mixture components. Figure 6 reveals relevant data characteristic for methanol, while Fig. 7 similar results for four other monohydric alcohols. Each of the relationships reveals a distinct maximum in the range of low alcohol concentrations and a minimum in the range of its high concentrations. The appearance of the maximum is related to the increase in the specific heat of the mixture in this region, up to a value exceeding the specific heat of water (as in Fig. 4). According to Table 1, it is one of the most characteristic features of hydrophobic liquids.

It can be noted that the deviation of effusivity from linearity for all investigated alcohols except methanol reaches a maximum at similar values of mass fraction, i.e. $1/(1 + m_w/m_{alc})$ = const, in the range of low alcohol concentrations and a minimum in the range of its high concentrations. In other words, for the three remaining alcohols the positions of these extrema seem to be related mainly with a total mass of the alcohol in the solution, irrespective of alcohol type. The experimental uncertainty of the relative deviation of thermal effusivity from linearity, $\Delta e/e_w$, was estimated as $\delta e = \pm 0.009$.

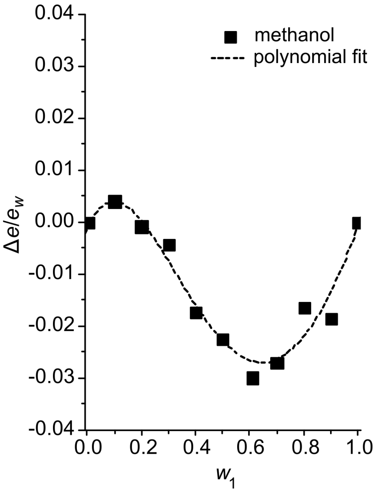

Fig. 6. Deviation of effusivity from linearity determined by photoacoustic measurements for the mixtures of methanol (Sikorska *et al.*, 2010).

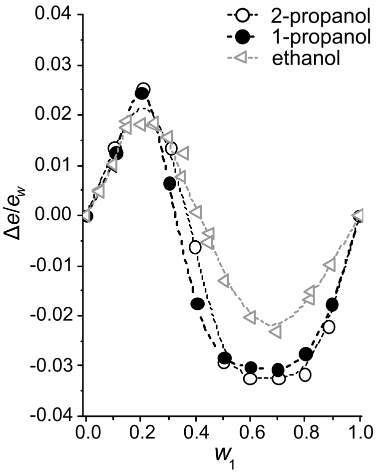

Fig. 7. Deviation of effusivity from linearity determined by photoacoustic measurements for the mixtures of different simple alcohols with water (relevant values of thermal conductivity were taken from Sikorska *et al.* (2010)).

3.4. Characteristic points in concentration dependence of selected thermodynamic parameters of aqueous mixtures of different monohydric alcohols

In Table 3, the positions of maxima of $\Delta e/e_w$ are compared with those corresponding to extrema of adiabatic compressibility, κ_s, which we investigated in our experiments. Moreover, Table 3 comprises also similar data for two thermodynamic functions characterizing the mixing of simple alcohols with water, i.e. excess enthalpy of activation ΔH^E and excess partial molar volume V_p^E. The location of extrema is given in units relevant for considered physical quantity, i.e. in mole fractions (compressibility, enthalpy, partial molar vol-

Table 3. Location of the $\Delta e/e_w$ maxima, in comparison with location of relevant extrema of adiabatic compressibility coefficient κ_s, excess enthalpy of activation $\Delta H^E(\tau_1)$ and excess partial molar volume V_p^E.

	$\Delta e/e_w$, max		κ_s, min	$\Delta H^E(x_1)$	V_p^E
	w_1	x_1	x_1	x_1	x_1
Methanol	0.10	**0.060**	0.137^b	0.12^c	0.22^f
Ethanol	0.20^a	**0.090**	0.100^a 0.100^d	0.08^c	0.09^f
1-propanol	0.20^a	**0.067**	0.050 0.045^d 0.050^e	0.06^c	0.07^f
2-propanol 2-propanol	0.21^a	**0.070**	0.060^a	0.07^c	–

[a] (Sikorska *et al.*, 2010), [b] (Ernst, Gliński, 1977), [c] (Sato, Buchner, 2005), [d] (Jerie *et al.*, 1986), [e] (Marczak, Spurek, 2004), [f] (Franks, 2000).

ume) or mass fractions (effusivity). To simplify the comparison, column 3 summarizes the conversion of the respective mass fractions to mole fractions (marked in bold font).

As can be seen from Table 3, the maximum deviation of effusivity from linearity for three of the investigated alcohols (except for methanol) is observed approximately for the same mass fraction of alcohol, $w_1 = 0.2$. Of course, the mole fractions corresponding to this concentration value are different for different alcohols. However, it should be pointed out that for each alcohol the location of the maximum effusivity deviation expressed as a mole fraction is very similar to the locations of maxima of characteristic excess thermodynamic functions: excess enthalpy of activation of collective component of dielectric relaxation process, $\Delta H^E(x_1)$, and excess partial molar volume of alcohol, V_p^E, in the mixture. Therefore, one may assume that they reflect the same physical cause, e.g. the effect of nonpolar CH_2 and CH_3 groups on the aqueous network reorganization time suggested by Sato and Buchner (2005). The concentration dependences for methanol, in contrast to other alcohols, do not comply with the above rules. This may possibly be caused by the already mentioned ability of methanol to form associates both as a pure alcohol as well as in mixture with water (Fig. 8).

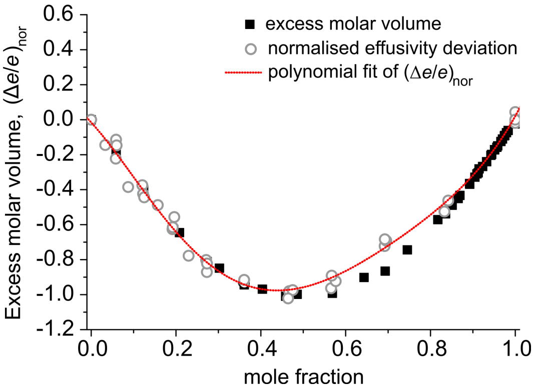

Fig. 8. Comparison of the deviation from linearity of effusivity and molar volume (obtained by density measurements) for the methanol-water mixture, as a function of the mole fraction.

The location of concentration dependence minimum of the function $\Delta e/e_w$ for other alcohols also corresponds approximately to the location of the minimum of the excess molar volume of the investigated mixture (Sikorska *et al.*, 2010).

The results of effusivity measurements and their analysis for different methanol concentrations in water-methanol mixtures enabled us to perform a comparison with similar data describing concentration dependences of other thermodynamic quantities characterizing water-methanol mixtures. The experimental investigation of effusivity deviation from linearity, examined as a function of methanol concentration, has confirmed earlier conclusion, formulated already for other aqueous mixtures of organic liquids, that this procedure is helpful in identification of interaction processes between mixture components. It has been shown that the obtained positive deviations of effusivity from linearity in aqueous solutions of alcohols at low concentrations can be assigned to hydrophobic interactions. Such interactions in alcohol solutions were confirmed in many research studies, for example the ones concerning investigation of volumetric (Jerie *et al.*, 1986), elastic (Marczak, Spurek, 2004), or dielectric (Sato, Buchner, 2005) properties. As it was validated by mass and IR spectrometry (Wakisaka, Matsuura, 2006), for higher concentrations, i.e. the ones exceeding concentration corresponding to the minimum of the effusivity deviation curve, the processes related to the formation of hydrogen bonds with water and association of alcohol molecules are predominant.

As it can be seen in Table 3, the excess molar volume minima are located at the same concentration as those of thermal effusivity. It seems therefore that effusivity deviation from linearity is a good indicator to identify such interactions between molecules in water mixtures. The discussed deviation turned out to be sensitive to hydrophobicity, which is of great importance in biology and medicine.

Effusivity is not frequently investigated physical quantity. The most interesting papers on this topic are the ones by Dadarlat *et al.* (2009). They concern similar studies of several liquids (Dadarlat, Pop, 2012), semi liquids (Bicanic *et al.*, 2004) and solids (Dadarlat *et al.*, 2009). Their effusivity measurement of liquid mixtures by the photoacoustic method allows the determination of its mean value over the so-called thermal diffusion length $\mu = \sqrt{\frac{\alpha}{\pi f}}$, where α is the thermal diffusivity of the sample and f is the light modulation frequency. Effusivity contains information on a product of the three quantities, ρ, λ, and c_p, determining the mean rate of heat exchange between the sample and the medium. This quantity, having a character of a thermal property is strictly related to dynamic processes occurring between the mixture components and can be an additional valuable source of information about these processes. Concentration dependence of effusivity of water solutions of methanol, likewise concentration dependences of many other quantities, including thermodynamic ones, does not follow the rules typical for other alcohols. A possible reason of this fact can be methanol molecules tendency to form associates. Photoacoustic method can also be used to determine, based on Eq. (1), other thermodynamic quantities of liquids or their mixtures, e.g. thermal conductivity.

In general, the discussed photoacoustic method appears to be a splendid research tool, competing with other techniques, such as acousto-optic and photoacoustic spectroscopy investigation (Sikorska *et al.*, 2006; 2005; 2001) along with the ultrasonic spectroscopy (Linde, Lezhnev, 2000; Linde, 1997; Linde *et al.*, 2010).

As far as the experimental method is concerned, it is necessary to conclude that both ultrasonic (Łabowski, Skrodzka, 1989) and photoacoustic spectroscopy are very useful in the investigations of chemical compounds, water and their mixtures.

4. Conclusions

We conclude that:

- The use of the photoacoustic measurement technique allows determination of thermal effusivity changes in binary mixtures of water and alcohols in relatively easily and accurate manner.
- The photoacoustic measurement technique does not cause significant thermal fluctuations inside a sample during measurements, and thus has a negligible effect on the investigated liquid structure.
- It has been shown that the obtained positive deviations of the effusivity from linearity in aqueous solutions of alcohols at low concentrations can be assigned to hydrophobic interactions.

We have shown that the photoacoustic method applied to study thermal dependence of effusivity on the molar concentration of the investigated substance is a powerful tool, complementary to other ultrasonic techniques commonly used to examine structural changes of liquid mixtures.

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