

## ULTRASONIC INVESTIGATION OF PSEUDO-STABLE STRUCTURES IN AQUEOUS MIXTURES OF POLYETHYLENE GLYCOL

C. E. H. Schmelzer<sup>+,\*</sup>, E. Rosenfeld<sup>+</sup>, and B. B. J. Linde<sup>#</sup>

<sup>+</sup> Dept. of Computer Science and Applied Natural Sciences, Fachhochschule Merseburg, Merseburg, Germany

<sup>#</sup> Institute of Experimental Physics, University of Gdańsk, Gdańsk, Poland

\* Present address: Department of Pharmacy, Martin-Luther-University Halle-Wittenberg, Germany  
schmelzer@pharmazie.uni-halle.de

### Abstract

The velocity of ultrasound ( $c$ ) and the density ( $\rho$ ) have been measured in mixtures of water and polyethylene glycol (PEG) in the temperature range from 288.15 to 328.15 K. Based on the data obtained, the adiabatic compressibility coefficient ( $\beta_{ad}$ ) has been calculated from Laplace's equation. The variations of  $c$ ,  $\rho$  and  $\beta_{ad}$  with concentration ( $\mu$ : mole fraction) and temperature have been studied. Structural interactions and the formation of a compact pseudo-stable structure in the region of a very low polyethylene glycol concentration have been reported. The structure built in these mixtures cannot be a liquid clathrate-like hydrate neither type I nor type II.

### Introduction

Aqueous solutions of nonelectrolytes have been known to exhibit some unusual behaviour in their physicochemical properties. The molecular structures and interactions of such solutions have been studied using ultrasonic investigations by many authors [1, 2, 5-7].

The determination of the velocity of ultrasound provides the possibility to calculate the coefficient of the adiabatic compressibility ( $\beta_{ad}$ ) in accordance with Laplace's equation (1)

$$\beta_{ad} = (\rho c^2)^{-1}, \quad (1)$$

where  $\rho$  is the density and  $c$  is the ultrasonic velocity of the liquid investigated.

The ultrasonic velocity and the adiabatic compressibility of dilute aqueous nonelectrolyte solutions show variations with concentration which are most frequently attributed to changes in their molecular structure.

In detail, dilute aqueous solutions of polar organic compounds usually show a region where the isotherms of the adiabatic compressibility plotted as a function of the mole fraction ( $\mu$ ) intersect before reaching minimum values. According to Baumgartner and Atkinson [1], the minima of the compressibility isotherms should be related to the formation of clathrate-like structures, whereas Endo [2] relates the formation of such a structure to the intersection of the compressibility isotherms. The presence of this point was attributed to structures type I and II [8, 2-4].

Clathrate hydrates are non-stoichiometric systems which can be described by the guest-host model. Water in liquid state which plays the role of the "host" is known to have a hexagonal ice-I structure with numerous cavities [4]. The guest molecules fill in the cavities of the framework of the liquid water structure. This change in structure leads to an enhancement of the water lattice. Prerequisite for this kind of mechanical inclusion is the presence of hydrophobic parts on the molecules of the solute.

However, less attention has been given to aqueous systems, where the solute has mainly hydrophilic parts. For such systems, the formation of a clathrate-like structure is energetically unfavourable and therefore not likely.

In the present paper, the attempt was made to examine the properties of this kind of aqueous system using polyethylene glycol.

### Experimental

Polyethylene glycol 1000 of analytical grade was used without further purification. Double distilled and degassed water was used to prepare the solutions. The ultrasonic velocities as well as the densities of these mixtures were measured over the entire concentration range and at temperatures between 288.15 and 328.15 K in intervals of 5 K (except for mixtures of higher PEG concentration which were already solid at lower temperatures).

#### Sound velocity

The propagation velocity was measured with accuracy better than  $\pm 0.02$  % using the automatic ultrasonic phase velocimeter MUP (ECOLAB, Poland).

#### Density

The densities were measured using the oscillating tube densitometer DMA 58 (Anton Paar GmbH, Austria). The accuracy was better than  $\pm 0.01$  %.

### Results and discussion

In Fig. 1, the isotherms of the ultrasonic velocity are plotted in dependence upon the concentration for aqueous mixtures of PEG 1000. The sound velocity isotherms plotted versus mole fraction of PEG intersect approximately at a common point ( $c_S$ ) before reaching maximum values ( $c_{max}$ ). The characteristic quantities are collected in Table 1.

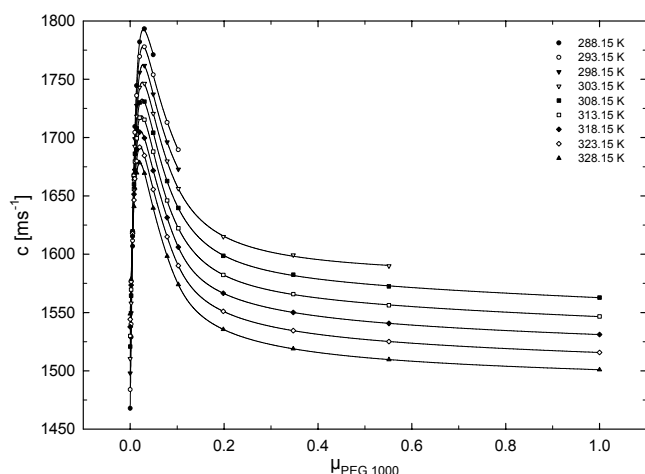


Figure 1: Ultrasonic velocity versus concentration of aqueous solutions of PEG 1000

Table 1: Data concerning sound velocity

$c_{max}/\text{ms}^{-1}$ ( $T=288.15\text{ K}$ )	$\mu(c_{max})$	$c_s/\text{ms}^{-1}$	$\mu(c_s)$
1793	0.030	1620	0.0055

Based on the ultrasonic velocities and densities determined, the adiabatic compressibility coefficients were calculated. In Fig. 2a, the adiabatic compressibility is plotted versus the mole fraction for aqueous solutions of PEG 1000. The curves have their compressibility minimum  $\beta_{ad,min}=2.8\text{ Pa}^{-1}\cdot 10^{-10}$  for a mole fraction of  $\mu=0.033$  and at a temperature of 288.15 K. For higher temperatures the minima shift slightly towards lower solute concentration.

Fig. 2b shows the compressibility isotherms for a small range of low PEG concentration. It can be seen that the compressibility isotherms for all measured temperatures also intersect approximately at a fixed concentration close to  $\mu=0.0044$ . The corresponding compressibility coefficient  $\beta_{ad,S}$  is approximately  $3.8\text{ Pa}^{-1}\cdot 10^{-10}$ .

To summarize, the aqueous mixtures of the polyethylene glycol 1000 exhibit the following characteristic features:

- (i) The isotherms of the adiabatic compressibility have minima in the concentration range from  $\mu=0.026$  to  $\mu=0.033$ . These minima shift to a lower concentration of PEG with increasing temperature.
- (ii) The isotherms intersect approximately at a common point corresponding to a fixed concentration. Therefore, one could assume that the adiabatic compressibility coefficient for the corresponding concentration is independent of temperature. However, in the strict sense, the intersections of the respective isotherms shift to a lower solute concentration with an increase in temperature.

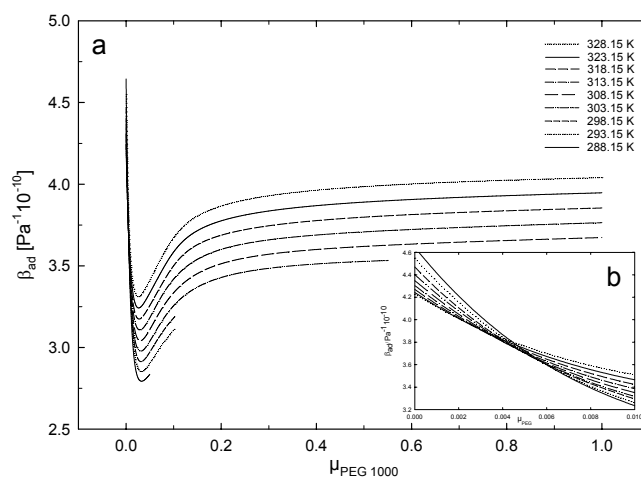


Figure 2: Adiabatic compressibility versus concentration (a - full and b - part) of PEG 1000 aqueous solutions

(iii) From the mole fraction of  $d\beta_{ad}/dT \approx 0$ , it follows a stoichiometry of 1 molecule PEG 1000 to about 226 water molecules.

### Conclusion

The presence of the minima of the adiabatic compressibility manifests the formation of pseudo-stable structures in the mixtures of polyethylene glycol and water.

Although an intersection point of the isotherms of the adiabatic compressibility as well as the compressibility minima have been found, which both are usually seen as indicators for the formation of a clathrate-like structure in liquid aqueous systems, the stoichiometry for  $d\beta_{ad}/dT \approx 0$  does not correspond with any of the known clathrate-like structures. Therefore, the structure can be neither of type I nor type II.

### Acknowledgement

This work was supported by the University of Gdańsk (KBN), projects grant BW 5200-5-0011-3.

### References

- [1] E. K. Baumgartner and G. Atkinson, "Ultrasonic Velocity in Nonelectrolyte-Water Mixtures," J. Phys. Chem., vol. 75, pp. 2336-2340, 1971.
- [2] H. Endo, "The Adiabatic Compressibility of Nonelectrolyte Aqueous Solutions in Relation to the Structures of Water and Solutions," Bull. Chem. Soc. Jpn., vol. 46, pp. 1106-1111, 1973.
- [3] M. von Stackelberg and H. R. Müller, "Feste Gashydrate II," Zeitschrift für Elektrochemie, vol. 58, pp. 25-39, 1954.
- [4] I. W. Matyasch, A. I. Toryanik and V. V. Kisel'nik, "O strukture rastvorov neelektrolitov," Zh. Strukt. Khim., 8, pp. 418-423, 1967.
- [5] A. Baranowski, K. Jerie, J. Gliński and K. Orzechowski, "Positron Annihilation in and Compressibility of Water-Organic Mixtures,"

- Journal of Radioanalytical and Nuclear Chemistry, vol. 190, pp. 469-473, 1995.
- [6] D. Sailaja, K. N. Raju, G. S. Santha Devi and K. Subbarangaiah, "Ultrasonic Behaviour of Aqueous Solutions of Polyethylene Glycols on the Temperature of Adiabatic Compressibility Minimum of Water," Eur. Polym. J., vol. 34, pp. 887-890, 1998.
- [7] B. Linde, E. Rosenfeld and A. Christ, "Acoustic Investigations of Water and 1,3-Dioxane Mixtures," Molecular and Quantum Acoustics, vol. 20, pp. 148-158, 1999.
- [8] D. W. Davidson: in "Water - Vol. 2, Water in Crystalline Hydrates Aqueous Solutions of Simple Nonelectrolytes," edited by F. Franks, Plenum Press, New York, London, pp. 115-133, 1973.