2aPAc3. Photo-acoustic and ultrasonic investigation of the mixtures of water and several glycols

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In the paper the results of the ultrasonic velocity and absorption measurements were presented, as well as the thickness in water mixtures of some glycols. The experiments were provided in the temperature range from 291.15 to 303.15 K for whole molar fraction. Adiabatic compressibilities were calculated from Laplace's equation based on the experimental results obtained. Variations of these values with concentration and temperature were studied. Structural interactions and the formation of a compact pseudostable structure at very low concentrations of ethylene glycol and polyethylene glycols were observed. The plots of the adiabatic compressibility versus the mole fraction of PEG and EG display two characteristic points at low concentrations: the intersection of the isotherms and their minimum. Such relations between adiabatic compressibility, concentration and temperature are usually attributed to the formation of pseudo-stable molecular structures. To formulate a model of local structures present in the investigated molecular systems it is indispensable to get an insight into hydration of molecules and the formation of hydrogen bonds.

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INTRODUCTION

To understand the concept of "aqueous structures" or the definition of "hydrogen bonds" it is necessary to elucidate the role of water in aqueous solutions. Accordingly, a model of interactions in aqueous solutions of polymers may be created. Such systems seem interesting in respect of the presence of both water and polymers, since in this case also the polymers become the object of investigations. Polyethylene glycol (PEG) has a simple molecular structure, OH-(CH2-CH2-O)n-H, and is a very good object for the investigation of structural effects due to the presence of hydrogen and etheric bonds that are capable of forming hydrogen bonds with water molecules. Another advantage of this polymer when examining the hydration of molecules is the dependence of its properties upon temperature and concentration of its water solutions. However, the most interesting is that PEG can adopt a helical structure [2]. In such a conformation, the distance between two neighbouring oxygen atoms (along the whole molecular chain) (2.88 Å) is very close to the length of O-O bond in liquid water (2.85 Å) [3].

When plotting the adiabatic compressibility coefficient versus the mole fraction, one can notice two characteristic points at low concentrations of the non-electrolytes examined, i.e. intersection of isotherms and their minimum. The regularities observed result from structural interactions attributed to the formation of clathrate-like structures of type I and II. Baumgartner and Atkinson [1] ascribed the minimum compressibility point to the formation of such structures, whereas according to Endo [4] such a packing of structures occurs at a concentration corresponding to the isotherm's intersection point. Acoustic investigations of polyethylene glycols 1000 and 1540 revealed a similar behaviour but the formation of clathrate compounds of type I or II by these substances was excluded [5, 6].

In the present paper we shall propose a model of molecular interactions in the systems of polyethylene glycols 200 and 400 and ethylene glycol, based on acoustic investigations in which hydration and the presence of hydrogen bonds were taken into account.

EXPERIMENTAL RESULTS AND ANALYSIS

The adiabatic compressibility coefficient has an extremum at a concentration of 0.14 for PEG 200, and 0.073 for PEG 400 solution. Based on the above results it can be calculated how many molecules of water are associated with one PEG molecule for assumed mole fractions. Polyethylene glycol 200 has a compressibility minimum when the ratio of the polymer to water amounts to about 1:6.1. In the case of PEG 400 this ratio equals 1:12.7. These results can be explained by the formation of hydrogen bonds between water and the oxygen atom from the ether bond when water is added to the polymer. Basically, each oxygen atom from the ether group can be an acceptor of two hydrogen bonds. In addition, oxygen atoms are also present at the ends of each polymer molecule.

In reports based on the IR spectral measurements [2] and diffraction of neutrons [3], several possible hydrogen bonds in similar molecular systems were suggested. One of the models proposed assumes that one water molecule is associated with two adjacent oxygen atoms of the ether groups. Taking such a position of hydrogen bridges into account, the number of water molecules necessary to form the first hydration layer can be calculated: 6 water molecules for PEG 200 and 11 for PEG 400. Such an amount of water is close to such concentrations of PEG 200 and 400 aqueous solutions at which the compressibility minimum was observed.

Characteristic minimum cannot be observed in practice for the system of ethylene glycol and water, probably due to the lack of ether bonds which, for example in the case of polyglycols and water, stiffen the whole system. Moreover with the increasing length of the molecule the minimum becomes sharper and more sensitive to concentration changes, shifting also towards lower polymer concentrations. Hence, the bigger the PEG molecule, the more stable its aqueous solution. When increasing gradually the amount of water in solution, apart from the compressibility minimum also the intersection point of isotherms can be observed.

The adiabatic compressibility coefficient corresponding to the intersection point of isotherms occurs at a concentration of 0.116 for the solution of EG, and 0.031 and 0.017 for solutions of PEG 200 and 400, respectively. Consequently, at points for which \( \frac{d\theta_{ad}}{dT} = 0 \), the stoichiometric ratio of ethylene glycol and water amounts to 1:7.6, for polyethylene glycol 200 to 1:31, and 1:58 in the case of polyethylene glycol 400.

In the investigations of long PEG polymers (called PEO), carried out based on the diffraction of neutrons [3, 7], it was found that two hydration regions could be determined in the hydration process. Stoichiometry of hydration was also estimated: 6 molecules of water were assigned to each PEO monomer. Considering the above, it is possible...
to calculate the stoichiometry of such a system: for PEG 200 the number of water molecules necessary for the interactions mentioned amounts to 26, 56 molecules are assigned to PEG 400, and 6 to EG.

CONCLUSIONS

Thus, an attempt can be made to formulate a thesis that the addition of water to pure polymer, causing the occurrence of a characteristic minimum on the plot of adiabatic compressibility versus concentration, results from the formation of the first hydration zone. This phenomenon is not observed for ethylene glycol due to the lack of sufficiently strong intermolecular interaction. As a result of further addition of water, the hydrated molecules "swell", the compressibility coefficient grows, and the system becomes more elastic. The intersection point of compressibility isotherms corresponds to the second hydration zone.

Taking into account the similarity of distances between successive oxygen atoms in the polymer, between oxygen atoms in liquid water and the results reported herein, a question arises as to which molecules in fact stiffen the system studied. Bearing in mind the discrepancies of results obtained for the solutions of ethylene glycol and polyethylene glycols, a conclusion can be drawn that those latter substances can stabilize the system.

In addition, it can be inferred from the results obtained that the polymers discussed do not occur as straight chains but as twisted helix-like structures, and their aqueous solutions are the more stable, the longer the PEG chain.

The experiment carried out has demonstrated that ultrasonic investigations are very useful in determination of molecular interactions and to determine their hydration.

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REFERENCES