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Hydration numbers of non-electrolytes – Application of the acoustic method of Pasynski

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Abstract

Applicability of the acoustic Pasynski method of determination of hydration numbers for non-electrolytic aqueous solutions has been tested and discussed. It was shown for dilute aqueous solutions of few homologous series of organic non-electrolytes that the hydration numbers are strongly and directly depending on the length of solute molecules and the groups which are their constituents. Thus, the results suggest that hydration is an additive parameter, although its mechanisms are different.

Keywords: Adiabatic compressibility; Aqueous solutions pf non-electrolytes; Hydration; Sound velocity; Hydration numbers; Hydrophobic hydration; Hydrophilic hydration

1. Introduction

Hydration phenomena, in particular the hydration numbers, structure of hydrates formed in aqueous solutions, and the effect of the solute on the structure of surrounding water has long been a subject of vivid interest in physics, chemistry and biological sciences [1]. This problem seems to be relatively simple for spherical ions, where the electrostatic interactions dominate in formation of the solvation sphere, although the effect of a solvate on the more distant solvent molecules is much less clear. However, the structures formed around more geometrically complex solutes, in particular organic and biological ones are the subject of many investigations, because hydration plays substantial role in the stability of and recognition between biologically important compounds [2–7]. In particular, the idea of hydrophobic hydration of Frank and Evans [8] should be also applied in these cases; see also a review on this concept and its consequences by Ruckenstein [9]. The next stage of considerations concerns more complicated molecules containing parts of different hydrophobicity, where the hydrophobic and hydrophilic hydration occur simultaneously; the examples are amino acids.

Among the experimental methods very well suited for investigating structure of liquids, the ultrasonic velocity is one of most promising, in particular if combined with density yielding the adiabatic compressibility coefficient – the quantity having well-defined thermodynamical meaning and obtainable with excellent accuracy. In this paper, we will prove that it is possible to obtain the hydration numbers of non-electrolytes from the compressibility data. Moreover, we will show that the hydration number obtained is almost linearly depending on the size of the solute molecule and the number and nature of its constituents.

2. Experimental

Solutions were prepared by weighing before measurements using doubly fresh-distilled water. Their compositions are given in mole fractions throughout this paper. All the chemicals were of quality sufficient to use them without additional purification.

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Sound velocity was determined using a computer-steered OPKUD 01/100/OPGUD (Optel, Poland) apparatus, with the absolute accuracy better then ±0.2 m/s and the precision of the same order. The device contains ultrasonic testing card, pulser, receiver and cuvette with transducers attached on its opposite sides. The card is controlled by the software, that finally calculates the sound speed. The cuvette is filled with measured fluid and the time is measured that sound needs to travel between the walls (in the fluid) and in the walls.

Density was determined using a vibrating tube Ecolab MG-2 (Kraków, Poland) apparatus with an accuracy better than $\pm 0.1\ \mathrm{kg\,m^{-3}}$. The idea of the measurement is based on that of Kratky et al. [10], i.e. the dependence of the free vibration frequency of a quartz tube on density of the medium filling it.

Temperature of the measurements was 25 °C ± 0.05, stabilized by a precision MLW UH (Germany) thermostat. Its stability was checked by a digital thermometer built in the density apparatus, and the absolute value by a mercury precision thermometer.

3. Results and discussion

Sound velocity can be determined with very good precision (typically better than ±0.5 m/s, while the sound velocity in pure water is about 1500 m/s at room temperature), the same concerns density. The Laplace equation combines these two quantities yielding the adiabatic compressibility coefficient, κ_S:

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S = \frac{1}{c^2 \cdot \rho} \tag{1}$$

where c is the sound velocity, ρ is the density; V is the volume, P is the pressure, and index S means adiabatic conditions.

κ_S parameter, resulting from the elastic properties of the medium, can be interpreted directly in terms of the structure of liquid. Thus, ultrasonic measurements are often applied in investigating the solvation phenomena of electrolytes, in aqueous [11] as well as in non-aqueous systems [12], including the mixed water + organic solvents [13]. For these systems the concept of Pasynski is applied [14] (see below for details). According to Pasynski, solvation should be manifested in decrease of compressibility when solute is added to the liquid. It is always observed for polar non-electrolytic solutes in water.

Table 1 collects the experimental results (the slopes of compressibility vs. solute mole fraction dependences, $\mathrm{d}\kappa_S/\mathrm{d}x_{\mathrm{solute}}$), as well as the resulting hydration numbers obtained from Pasynski relation (see below for details of calculations). It should be stressed that all the dependences $\kappa_S = f(x_{\mathrm{solute}})$ are perfectly linear, at least in the limits of the (rather low) experimental error. Thus, the slopes of the latter could be calculated by fitting the first order polynomial only. The example of experimental results is given in Fig. 1.

The maximum solute concentrations were very low, rarely exceeding the mole fraction of 0.01. The first and important observation is the perfect linearity of compressibility with composition, apparently in contradiction with the well known parabolic-like $\kappa_S = f(x_{\mathrm{solute}})$ dependences for aqueous non-electrolytes [15] which, evidently, is observed only in higher concentrations. This is easy to understand, however, if only one assumes that in diluted systems of this kind the hydration processes are “pure”, i.e. no competition of well-separated hydrates occurs for solvent molecules.

The second observation, already mentioned. is also of great importance for our further considerations. Water is characterized by relatively low compressibility, when compared to other liquids with low molecular masses (at room temperature ca. $4.48 \cdot 10^{-10}\ \mathrm{m^2/N}$, compared to about $7 \cdot 10^{-10}$ for CCl_4 [16] or $10 \cdot 10^{-10}$ for short-chained alcohols and alkanes [15]). However, addition of non-electrolytes to water always results in the initial linear decrease of compressibility, the bigger solute molecule the stronger [17].

As mentioned above, the compressibility data were used to calculate the hydration numbers according to the formula first derived by Pasynski [14]

$$n_h = \frac{n_{H_2O}}{n_{\mathrm{solute}}}\left(1 - \frac{\kappa_{\mathrm{solution}}}{\kappa_{H_2O}}\right) \tag{2}$$

where n_i is the number of moles of species i in solution, and κ is the compressibility (or compressibility coefficient).

The assumption of this formula is very simple: hydration means that after addition of a solute there are molecules of water which become non-compressible because they are now bonded to the guest molecule; remember that bonding means for chemists a shortening of the distance between interacting moieties and formation of rigid link between them. Thus, a number of water molecules becomes excluded from the total compressibility. Originally, Pasynski applied this idea to electrolytic solutions, supposing that water molecules undergo electrostrictive compression in electrostatic field of ions, which acts like very high static pressure and makes them less compressible (or even non-compressible at all).

There were also other attempts to engage the acoustic method to aqueous non-electrolytes [18–20], where the shift of the maximum of sound velocity plotted vs. temperature with addition of a solute was interpreted in terms of engaging water in hydration. The foundations of these efforts are different from these of Pasynski and their applicability to real systems is not obvious. Also the results are rather far from expectations and the hydration numbers obtained, n_{h}, are too low.

Is it reasonable to treat diluted aqueous solutions of non-electrolytes very different than those of electrolytes? The interactions between water and a solute lead in both cases to the same final result: independent on the fact if electrostriction caused by electrostatic forces occurs or if hydrogen or other bonds are created, the local structure