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Hydration Numbers of Non-Electrolytes in Aqueous Solvents of Fixed pH

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Abstract In the present article the applicability of the Pasynski method of determination of hydration numbers of simple organic compounds in aqueous solvents of fixed pH at 25 °C from speed-of-sound and density measurements is tested and discussed. It was shown that for solutes which do not undergo protolytic reactions with a solvent the resulting values of hydration numbers are independent on the system pH—for these solutes n_h can be determined both in pure aqueous solutions and in mixtures containing ions. For solutes which undergo reactions with an acid or base, the Pasynski method yields hydration numbers which are a combination of compressibilities of substrates and products of occurring reactions.

Keywords Adiabatic compressibility · Hydration numbers · Non-electrolytes · Pasynski method · Speed of sound

1 Introduction

The structure of aqueous solutions of electrolytes and non-electrolytes is one of the most important questions of contemporary theory of liquids, in particular with reference to biology, biophysics, and environmental chemistry. The structure of water

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Dedicated to Professor Stefan Ernst on the Occasion of his 75th Anniversary. Professor Stefan Ernst is the quintessential definition of a physicochemist as well as of a tutor. He has been involved in physical chemistry from the very beginning of his scientific career, starting in electrochemistry and afterwards turning towards molecular acoustics. We have been always appreciated how he taught us all to be responsible researchers. Now we offer him our heartfelt congratulations. Best wishes for a wonderful 75th Birthday Celebration!

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and its influence on mechanisms of reactions occurring in water belong to the most interesting problems of contemporary science.

Natural biochemical systems are very complicated, and because of that, in physicochemical investigations simple two- or three-component models are used. Such model system studies have two advantages. First, microscopic interpretation of experimental data derived from studies on low molar mass compounds is relatively easy. Second, model studies readily allow one to systematically alter the structure, by using homological series, so that the contribution of a chosen atomic group can be assessed [1].

The adiabatic compressibility coefficient is known as an effective (in the sense of its wide application in investigating the structural aspects) probe for investigating the structural aspects of liquid systems [2–4], including such complicated ones as solutions of biologically active proteins [5,6]. Compressibility measurements find also particular applications in determining hydration numbers. The decrease of the compressibility with increasing concentration of a solute is usually attributed to electrostriction, although water involved in the “cages” surrounding the hydrophobic parts of molecules is also less compressible than the bulk one [7].

Independent of possible mechanisms of hydration, according to Pasynski the estimation of hydration numbers from a decrease of the compressibility with the addition of a solute can be applied both for electrolytic [8] and non-electrolytic solutes [9] in water.

In the present study we report hydration numbers of homological series of *n*-alcohols, *n*-amines, and normal carboxylic acids determined by the acoustic Pasynski method in water and in aqueous 0.2 M HCl and NaOH solutions at 25 °C.

2 Measurements

2.1 Chemicals

Methanol (J.T. Baker, The Netherlands, >99.8 %), ethanol (POCh, Poland, p.a. 99.8 %), *n*-propanol (Chempur, Poland, p.a.), *n*-butanol (POCh, Poland, pure), *n*-pentanol (Fluka, Switzerland, p.a.), ammonia solution 25 % (Eurochem BGD, Poland, p.a.), methylamine solution 40 % (Veb Laborchemie Apolda, Germany, pure), ethylamine solution 70 % (Merck, Germany, for synthesis), *n*-propylamine (Fluka, Switzerland, >98 %), *n*-butylamine (Fluka, Switzerland, ≥97 %), *n*-pentylamine (Fluka, Switzerland, >98 %), formic acid (AppliChem, Germany, p.a. 98 % to 100 %), acetic acid (Chempur, Poland, p.a. >99.5 %), *n*-propanoic acid (Merck, Germany, for synthesis, >99 %), *n*-butanoic acid (Merck, Germany, for synthesis >99 %), *n*-pentanoic acid (Reachim, Russia, pure), *n*-hexanoic acid (Fluka, Switzerland, p.a.), *n*-nonanoic acid (General Purpose Reagent BDH Chemicals Ltd Poole, England, >99 %), ammonium chloride (POCh, Poland, p.a.), methylamine hydrochloride (ABCR, Germany, 99 %), ethylamine hydrochloride (Fluka, Switzerland, ≥98 %), *n*-propylamine hydrochloride (ABCR, Germany, 98 %), *n*-butylamine hydrochloride (ABCR, Germany, 98 %), *n*-hexylamine hydrochloride (ABCR, Germany, 98 %), sodium formate (Odczynniki sp. zo.o., Poland, p.a. >99 %), sodium acetate (POCh, Poland, p.a. 99 % to 100 %), sodium *n*-propanoate (Alfa Aesar, Germany, 99 %), and sodium *n*-butanoate (Alfa Aesar, Germany, >98 %) were used without additional purification. Exact contents of ammonia, methylamine, and ethylamine in the samples were determined by titration. Water used was fresh-prepared, doubly distilled.

There were three series of experiments performed, differing by solvent: pure water, 0.2 M HCl, and 0.2 M NaOH. The two latter were prepared using Fixanal® chemicals. Samples were prepared by weighing a solute and the respective solvent shortly before measurements.

2.2 Procedures

The speed-of-sound was determined using a computer-controlled OPKUD 01/100 (Optel, Wrocław, Poland) apparatus, with an uncertainty better then 0.2 $\mathrm{m\cdot s^{-1}}$ and a precision of similar order. Measurements are based on the determination of the time an acoustic signal needs to pass through the sample of known length. The density was measured using a vibrating tube Ecolab MG-2 (Kraków, Poland) apparatus with an uncertainty of ca. 0.1 $\mathrm{kg\cdot m^{-3}}$.

The measurements were performed at $(25 \pm 0.01)\,^{\circ}\mathrm{C}$, stabilized by a precision Julabo F25-ME (Germany) thermostat. Its stability was controlled by a digital thermometer built-in the density apparatus, and its absolute value was determined by a precision mercury thermometer.

From the speed-of-sound and density data, the adiabatic compressibility coefficients, κ_S, were calculated, using the Laplace equation,

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

where V is the volume, P is the pressure, d is the density, u is the speed-of-sound, and the index S denotes adiabatic condition.

The relative change of compressibility was assumed by the bounding of water in hydration spheres, where they become incompressible. This leads to the well-known formula for the hydration number, n_h, known as the Pasynski equation [8,9] (see also a review by Stuehr and Yeager [10]):

$$n_\mathrm{h} = \frac{n_1}{n_2}\left(1 - \frac{\kappa_S}{\kappa_S^0}\right) \tag{2}$$

where n_1 and n_2 are the numbers of moles of water and solute in solution, respectively, κ_S is the adiabatic compressibility coefficient of the solution, and κ_S^0 is that of the pure solvent. The applicability of the Pasynski equation for non-electrolytic aqueous solutions was recently examined by us [11].

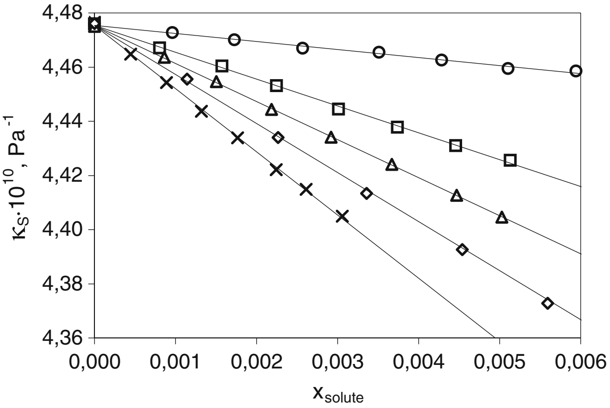

Fig. 1 Example of experimental results: plots of κ_S versus solute mole fraction for alcohols in water at 25 °C: ○ methanol, □ ethanol, △ *n*-propanol, ◇ *n*-butanol, × *n*-pentanol

3 Results and Discussion

Only very dilute systems were investigated in the present work. The mole fraction of solutes never exceeded 0.01, i.e., there were at least 100 water molecules per one solute molecule. Therefore, one can assume that no significant interactions occur between the solute molecules, the same concerns interactions between water molecules belonging to two different solvation clouds.

It is worth noting that—in the investigated range of concentrations—each of the solutes gives a perfectly linear dependence of the compressibility κ_S on concentration (R^2 coefficient was never lower than 0.999) at least within the limits of the experimental error (see Fig. 1), which is rather low. This means that the hydration numbers obtained from Eq. 2 remain undoubtedly constant at low concentrations.

The hydration numbers calculated from experimental data for investigated homological series of non-electrolytes in pure water, 0.2 M HCl, and 0.2 M NaOH at 25 °C are collected in Table 1 and depicted in Figs. 2, 3, and 4.

For solutes which do not undergo protolytic reactions with an acid or base, no significant difference was observed between hydration numbers determined in water and another solvent—see Table 1 and Fig. 2. However, this is not true for, as an example, *n*-amines in HCl (Fig. 3) or—to a much greater extent—for carboxylic acids in NaOH (Fig. 4).

The values of hydration numbers of *n*-amines in 0.2 M HCl are on average higher by about 1 than those in pure water. The hydration numbers of carboxylic acids in alkaline solutions are much lower than in pure water; moreover, hydration numbers of formic and acetic acids in 0.2 M NaOH solutions are negative.

To explain this, we determined the hydration numbers of *n*-alkylamines hydrochlorides and sodium salts of normal carboxylic acids from speed-of-sound and density experimental data. We also used the former results listed in the papers of Allam and Lee [12,13], who also employed the acoustic Pasynski method at 25 °C. The reason was the large number of simple electrolytes collected, resulting in reliable calculations

Table 1 Hydration numbers, n_h, of investigated non-electrolytes in water, 0.2 M HCl, and 0.2 M NaOH calculated using Eq. 2 at 25 °C

Solute	In water	In 0.2 M HCl	In 0.2 M NaOH
Methanol	0.7	0.6	0.6
Ethanol	2.2	1.6	1.7
n-Propanol	3.2	2.9	2.9
n-Butanol	4.1	3.8	3.7
n-Pentanol	5.2	5.2	5.4
Ammonia	1.1	2.3	0.8
Methylamine	1.7	3.3	1.7
Ethylamine	3.2	3.6	3.0
n-Propylamine	3.7	4.7	3.7
n-Butylamine	4.6	5.9	4.7
n-Pentylamine	5.5	7.0	5.5
n-Hexylamine	–[a]	7.5	–[a]
Formic acid	1.2	1.4	−3.7
Acetic acid	1.8	1.6	−0.6
n-Propanoic acid	2.7	2.9	1.3
n-Butanoic acid	3.5	3.9	2.6
n-Pentanoic acid	4.9	4.7	3.4
n-Hexanoic acid	–[a]	–[a]	4.3
n-Nonanoic acid	–[a]	–[a]	6.1

[a] Lack of experimental data for *n*-hexylamine in water and 0.2 M NaOH, and *n*-hexanoic and *n*-nonanoic acids in water and 0.2 M HCl because these solutes are almost insoluble in these solvents

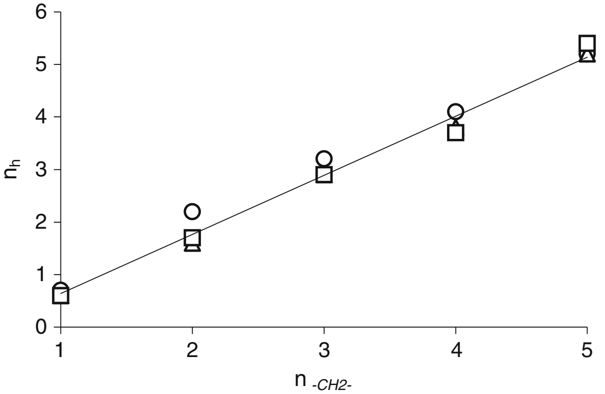

Fig. 2 Hydration numbers of investigated *n*-alcohols in water (◯), 0.2 M HCl (△), and 0.2 M NaOH (☐) as function of the number of –CH_2– groups in the alkyl chain of solute molecule at 25 °C. *Line* is drawn only to guide the eye

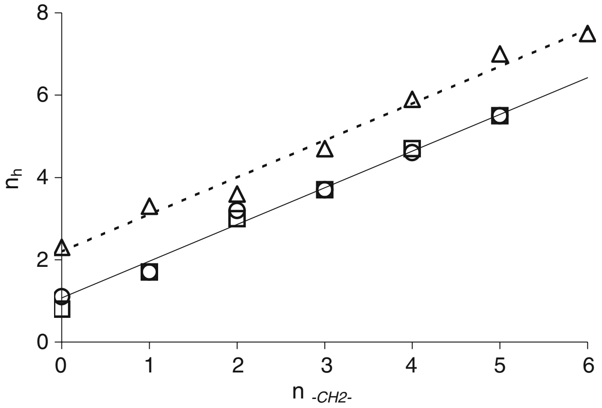

Fig. 3 Hydration numbers of investigated *n*-amines in water (◯), 0.2 M HCl (Δ), and 0.2 M NaOH (☐) as function of the number of –CH_2– groups in the alkyl chain of solute molecule at 25 °C. *Lines* are drawn only to guide the eye

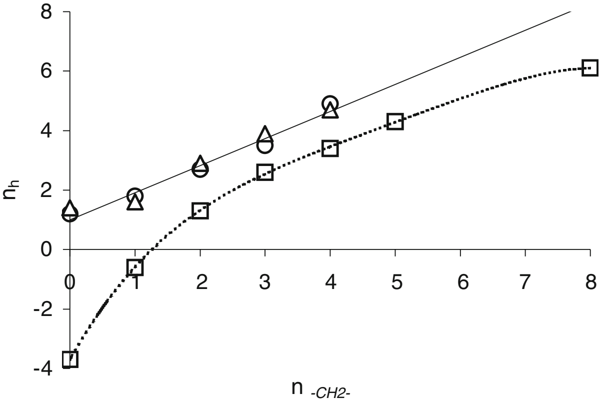

Fig. 4 Hydration numbers of investigated normal carboxylic acids in water (◯), 0.2 M HCl (Δ), and 0.2 M NaOH (☐) as function of the number of –CH_2– groups in the alkyl chain of solute molecule at 25 °C. *Lines* are drawn only to guide the eye

of the values of the hydration numbers of simple inorganic ions—the calculated values are listed in [14].

For example, n_h of sodium formate should be a sum of those of Na^+ cation and $HCOO^-$ anion. Knowing values of n_h of Na^+ (4.0) and Cl^- (3.1), we calculated hydration numbers of *n*-alkylammonium cations and carboxylic anions. The results of such theoretical estimations are collected in Table 2.

To explain that values of hydration numbers of *n*-amines in 0.2 M HCl are higher by about 1 than those in pure water, one should consider the following reaction:

$$RNH_2 + H^+ + Cl^- \rightarrow RNH_3^+\,Cl^- \qquad (3)$$

Table 2 Hydration numbers, n_{h} , of investigated organic electrolytes in water calculated using Eq. 2 (column 1) and hydration numbers attributed to *n*-alkylammonium cations and carboxylic anions (column 2) at 25 °C

Solute	$n_{\mathrm{h\ salt}}$	Ion	$n_{\mathrm{h\ RNH_3^+}}/n_{\mathrm{h\ RCOO^-}}$
Ammonium chloride	4.2	Ammonium	1.1
Methylamine hydrochloride	5.1	Methylammonium	2.0
Ethylamine hydrochloride	5.8	Ethylammonium	2.7
n-Propylamine hydrochloride	6.9	*n*-Propylammonium	3.8
n-Butylamine hydrochloride	7.9	*n*-Butylammonium	4.8
n-Hexylamine hydrochloride	9.7	*n*-Hexylammonium	6.6
Sodium formate	6.9	Formate	2.9
Sodium acetate	9.0	Acetate	5.0
Sodium *n*-propanoate	10.6	*n*-Propanoate	6.6
Sodium *n*-butanoate	11.6	*n*-Butanoate	7.6

This means that when amine is added to HCl solution, a reaction of RNH_2 with H^+ ions takes place. As a result of this reaction, RNH_3^+ cations appear in solution, and simultaneously the equivalent number of H^+ ions disappear in the system, while the number of Cl^- anions remains unchanged.

So, if taking the above into consideration, i.e., making a balance of water molecules engaged in the process of formation of ions and their solvates, the hydration numbers of *n*-amines in 0.2 M HCl solution can be calculated from the following equation:

$$n_{\mathrm{h\ RNH_2}}^{0.2\,\mathrm{M\ HCl}} = n_{\mathrm{h\ RNH_3^+}} - n_{\mathrm{h\ H^+}} \tag{4}$$

where $n_{\mathrm{h\ RNH_2}}^{0.2\,\mathrm{M\ HCl}}$ is the hydration number of *n*-amine in 0.2 M HCl, $n_{\mathrm{h\ RNH_3^+}}$ is the hydration number of the *n*-alkylammonium cation in pure water, and $n_{\mathrm{h\ H^+}}$ is the hydration number of the H^+ cation ($n_{\mathrm{h\ H^+}} = -1.0$, see [14]).

The results of such theoretical calculations shown in Fig. 5 and collected in Table 3 present a very good reproduction of hydration numbers of *n*-amines in 0.2 M HCl aqueous solutions.

In a similar way we can explain why the values of hydration numbers of normal carboxylic acids in 0.2 M NaOH solutions are lower than their values in pure water and become (apparently) negative for formic and acetic acids. Let us consider the following reaction:

$$\mathrm{RCOOH} + \mathrm{OH^-} + \mathrm{Na^+} \rightarrow \mathrm{RCOO^-} + \mathrm{H_2O} + \mathrm{Na^+} \tag{5}$$

In this reaction the $RCOO^-$ anions appear in solution, the equivalent number of OH^- ions disappear from the system, and the number of Na^+ cations remains unchanged.

When making a balance of water molecules engaged in the process of formation of ions and their solvates, the hydration numbers of carboxylic acids in 0.2 M NaOH solution can be calculated as follows:

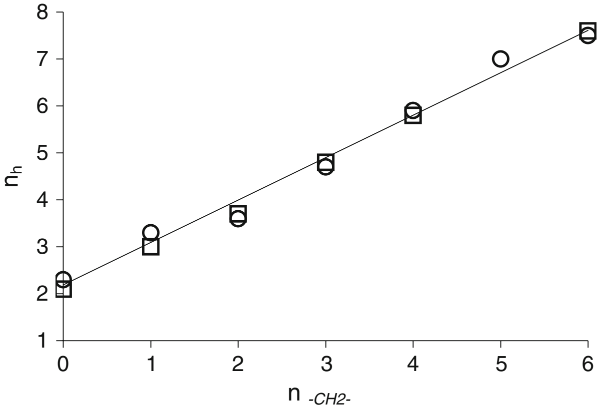

Fig. 5 Comparison of experimental (○) and calculated using Eq. 4 (□) hydration numbers of investigated *n*-amines in 0.2 M HCl at 25 °C. *Line* is drawn only to guide the eye

Table 3 Comparison of experimental and calculated (using Eq. 4) hydration numbers of investigated *n*-amines in 0.2 M HCl at 25 °C

Solute	$n_{\mathrm{h\ RNH_2}}^{\mathrm{0.2\,M\ HCl}}$	
	Experimental	Calculated
Ammonia	2.3	2.1
Methylamine	3.3	3.0
Ethylamine	3.6	3.7
n-Propylamine	4.7	4.8
n-Butylamine	5.9	5.8
n-Pentylamine	7.0	–
n-Hexylamine	7.5	7.6

$$n_{\mathrm{h\ RCOOH}}^{\mathrm{0.2\,M\ NaOH}} = n_{\mathrm{h\ RCOO^-}} - n_{\mathrm{h\ OH^-}} \tag{6}$$

where $n_{\mathrm{h\ RCOOH}}^{\mathrm{0.2\,M\ NaOH}}$ is the hydration number of carboxylic acid in 0.2 M NaOH solution, $n_{\mathrm{h\ RCOO^-}}$ is the hydration number of carboxylic anion in pure water, and $n_{\mathrm{h\ OH^-}}$ is the hydration number of OH^- anion ($n_{\mathrm{h\ OH^-}} = 5.9$, see [14]).

The results of such theoretical calculations shown in Fig. 6 and collected in Table 4 present again very good reproduction of hydration numbers of normal carboxylic acids in 0.2 M NaOH aqueous solutions.

4 Conclusions

Speed-of-sound and density data are used to determine the hydration numbers of *n*-alcohols, *n*-amines, and normal carboxylic acids in pure water and in aqueous solutions of 0.2 M HCl and 0.2 M NaOH. These values are very close to the literature n_h's obtained by the same technique, and of the same order as those obtained

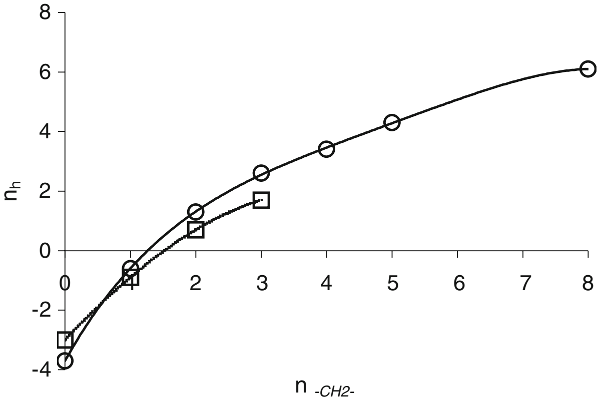

Fig. 6 Comparison of experimental (◯) and calculated using Eq. 6 (☐) hydration numbers of investigated normal carboxylic acids in 0.2 M NaOH at 25 °C. *Lines* are drawn only to guide the eye

Table 4 Comparison of experimental and calculated (using Eq. 6) hydration numbers of investigated normal carboxylic acids in 0.2 M NaOH at 25 °C

Solute	$n_{\text{h RCOOH}}^{0.2\text{ M NaOH}}$	
	Experimental	Calculated
Formic acid	−3.7	−3.0
Acetic acid	−0.6	−0.9
n-Propanoic acid	1.3	0.7
n-Butanoic acid	2.6	1.7
n-Pentanoic acid	3.4	–
n-Hexanoic acid	4.3	–
n-Nonanoic acid	6.1	–

by other methods. It was shown that the Pasynski method yields the same values of hydration numbers for solutes which do not undergo chemical reactions with solvent, that means the acoustic Pasynski method can be applied both in pure aqueous solutions and in mixtures containing neutral ions without any modifications or additional assumptions. On the contrary, for reacting systems the Pasynski method yields hydration numbers which result from compressibility of substances engaged in occurring reactions.

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