CHEMICAL REVIEWS

REVIEW

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Hydration Numbers of Nonelectrolytes from Acoustic Methods

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1. INTRODUCTION

Although the values of hydration numbers of guest molecules in aqueous solution are extremely important parameters necessary when discussing aspects of both intermolecular interactions and phenomena occurring at interfaces, for example, biological membranes,[1−4] for nonelectrolytic solutes these data are widely dispersed in the literature, and no review in this field has been published yet, other than for electrolytic solutions.[5−10] So, the aim of this work is to fill this gap. Because of the large number of papers devoted to this subject, we have limited its scope to include only the group of experimental methods that are based on the acoustical properties of matter and, in particular, measurement of the speed of sound.

To avoid misunderstanding, a definition of hydration number should be proposed first. It seems rather clear that no exact definition is possible. First, there are different types of interactions that lead to enforcement of local intermolecular attractions. Hydrophilic interactions, for instance, are closer in their nature to typical chemical bonds. On the other hand, hydrophobic hydration leads to increased local rigidity of the host water network, but the macroscopic effect is nearly impossible to distinguish from that caused by hydrophilic hydration. On the other hand, even for the apparently simplest situation, that is, a radial, uniform interaction, the effect of solute on the surrounding medium is described by an exponential function that is not known exactly; in such a case, the hydration number has to be defined as the number of water molecules located at a distance that is arbitrarily defined. Consequently, for simplicity's sake, we propose a working definition of hydration number as follows: the average number of water molecules that are affected by interactions between the solute and solvent and cause an observable effect on a physical property of the solution. For acoustic methods this physical property is usually compressibility.

2. ACOUSTIC METHODS FOR DETERMINATION OF HYDRATION NUMBERS OF NONELECTROLYTES

In general, the acoustic methods applied when determining the solvation numbers are based on exploiting the adiabatic compressibility coefficient, a parameter that can be easily and very precisely calculated from Laplace's equation:

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

where κ is the compressibility coefficient, ρ is the density, u is the speed of sound, index S denotes the adiabatic condition, and other symbols have their usual meaning. The link between compressibility and solvation is very intuitive: solvation involves a strong force field in which the solute molecules are placed and thus acts the same as pressure. While compressibility decreases with pressure because the decreasing intermolecular distances result in an increase in the intermolecular forces of repulsion, the limit of compressibility with pressure should be zero. Obviously,

Received: April 13, 2011
Published: December 09, 2011

Table 1. Hydration Numbers of Alcohols and Glycols at 25 °C

	method						
		Yasunaga					
solute	Pasynski	water + methanol	water + ethanol	water + propan-1-ol	water +2-methyl propan-2-ol	water + THF	nonacoustic methods
hydrogen peroxide	0.9$^{73-75}$						1.2,^{c,154} 0.91–0.93^{c155}
methanol	1,$^{a\ 12}$ 0.7$^{73-76}$	5.2^{121,122,127}	3.0,^{122} 3.2^{124,127}	2.7,^{122} 2.8^{124,127}	2.5^{122}	3.7^{124,127}	0.9–1.3,$^{c\ 154}$ 0.73–0.93,$^{c\ 155}$ 15,$^{d\ 156}$ 12,$^{e\ 157}$ 5.8,$^{f\ 157}$ 1.7,$^{g\ 158}$ 1.8–2.5,$^{a,h\ 159}$ 2.4$^{a,h\ 160}$
ethanol	3,$^{a\ 12}$ 2.16,$^{a,b\ 26}$ 2.2$^{73-76}$	10.8,^{121} 10.0^{122}	8.4^{122,124,127}	8.3,^{122} 8.8^{124,127}	8.0^{122}	10.2^{124,127}	1.44–1.48,$^{c\ 155}$ 15,$^{e\ 157,161}$ 10.5,$^{f\ 157}$ 10.3,$^{f\ 161}$ 4.0–4.5,$^{a,h\ 159}$ 4.5,$^{a,h\ 160,162}$
ethane-1,2-diol	4,$^{a\ 12}$ 3.6,^{a48} 2.3$^{73-75}$	5.9^{121}	2.7^{124,127}	1.9^{124}		3.1^{124}	1.8,$^{c\ 154}$ 16,$^{e\ 157,161}$ 5.7,$^{f\ 157}$ 5.6,$^{f\ 161}$ 2.2–2.7,$^{a,h\ 159}$ 0.60$^{q\ 163}$
propan-1-ol	3–4,$^{a\ 12}$ 3.38,$^{a,b\ 26}$ 3.2$^{73-76}$	16.5^{121,122}	14.8,^{122} 15.8^{124,127}	19.0,^{122} 19.9^{124,127}	18.1^{122}	21.4^{124,127}	0.60–0.80,$^{c\ 155}$ 17,$^{e\ 157,161}$ 14.1,$^{f\ 157,161}$ 6.2–6.5,$^{a,h\ 159}$ 6.7,^{a,h160} 12–13$^{i\ 164}$
propan-2-ol	3.58,$^{a,b\ 26}$ 3.2^{73,74}		14.3^{124,127}	16.2^{124}		17.7^{124}	2.10–2.50,$^{c\ 155}$ 17,$^{e\ 157,161}$ 16.4,$^{f\ 157}$ 15.8,$^{f\ 161}$ 6.7–7.1,$^{a,h\ 159}$ 7.2$^{a,h\ 160}$
2-methylpropan-1-ol		22.1^{121}	23.0^{127}				19,$^{e\ 157}$ 17.2,$^{f\ 157}$ 10.5–10.8,$^{a,h\ 159}$ 11.0$^{a,h\ 160}$
2-methylpropan-2-ol	4.9^{73,74}	22.4^{121}	21.0^{127}		22.6^{122}		19,$^{e\ 157}$ 22.7,$^{f\ 157}$ 13.2–13.5,$^{a,h\ 159}$ 13.2,$^{a,h\ 160}$ 28,$^{j\ 165,166}$ 20–25,$^{k\ 167}$ 24$^{j\ 168}$
propane-1,2-diol	3.7$^{73-75}$		6.9^{124,127}	6.3^{124,127}		8.3^{124,127}	
propane-1,3-diol	2.8^{73,75}		4.2^{127}				18,^{e157,161} 10.3,^{f157} 10.2^{f161}
propane-1,2,3-triol	4.35,$^{a\ 67}$ 4.0^{73,75}	5.3,^{121} 5.0^{122}	2.0,^{122} 2.9^{124,127}	2.0,^{122} 1.9^{124}	2.1^{122}	3.4^{124}	1.9–2.1,$^{c\ 154}$ 0.5,^{l154} 1.94–2.17,$^{c\ 155}$ 3.3,$^{q\ 163}$ 0.9–1.0$^{m\ 169}$
butan-1-ol	4.1$^{73-76}$	22.6,^{121} 23.1^{122}	23.5^{122,127}	38.7^{122}	38.0^{122}		20,$^{e\ 157}$ 17.1,^{f157} 5.3,$^{g\ 158}$ 10.5–11.0,$^{a,h\ 159}$ 10.7$^{a,h\ 160}$
butan-2-ol		21.3^{121}	21.7^{127}				4.90,$^{c\ 155}$ 19,$^{e\ 157}$ 18.8,$^{f\ 157}$ 11.6–11.8,$^{a,h\ 159}$ 12.4$^{a,h\ 160}$
3-methylbutan-1-ol							15.0$^{a,h\ 160}$
2-methylbutan-2-ol		27.9^{121}					14.7–15.0$^{a,h\ 159}$
butane-1,2-diol	4.7$^{73-75}$						
butane-1,3-diol	4.0^{73,75}		7.6^{124,127}	7.0^{124,127}		8.0^{124,127}	
butane-1,4-diol	3.7^{73,75}		6.3^{124,127}	4.9^{124}		6.9^{124}	1.49,$^{c\ 155}$ 21,$^{e\ 157}$ 14.0$^{f\ 157}$
butane-2,3-diol	4.8^{73}		9.3^{124,127}	9.2^{124}		11.3^{124}	
pentan-1-ol	5.2$^{73-76}$						22,$^{e\ 157}$ 19.4$^{f\ 157}$
pentane-1,2-diol	5.6^{73,75}						
pentane-1,5-diol	4.5^{73,75}						23,$^{e\ 157}$ 18.4$^{f\ 157}$
hexane-1,6-diol	5.4^{73,75}		12.0^{127}				25,$^{e\ 157}$ 20.1$^{f\ 157}$
2-ethylhexane-1,3-diol	8.2^{73}						
cyclohexanol	1.9$^{r\ 69}$	25.4^{121}					33$^{d,r\ 69}$
cyclohexane-1,2-diol	2.7$^{r\ 69}$						38$^{d,r\ 69}$
cyclohexane-1,4-diol	3.8$^{r\ 69}$						37$^{d,r\ 69}$
2-methoxyethanol			7.8^{127}	6.7^{127}			
2-ethoxyethanol			12.3^{127}				
2-butoxyethanol							23.7$^{n\ 170}$
1,4-cyclohexanedimethanol							5$^{o,p\ 171}$

Table 1. Continued

	method						
		Yasunaga					
solute	Pasynski	water + methanol	water + ethanol	water + propan-1-ol	water +2-methyl propan-2-ol	water + THF	nonacoustic methods
1,4-cyclohexanediol							5$^{o,p\ 171}$
1,3-dihydroxybenzene	2$^{a\ 12}$						
2-fluoroethanol							15,$^{e\ 161}$ 5.6$^{f\ 161}$
2,2,2-trifluoroethanol							16,$^{e\ 161}$ 10.2$^{f\ 161}$
2-chloroethanol							17,$^{e\ 161}$ 8.9$^{f\ 161}$
2,2-dichloroethanol							18,$^{e\ 161}$ 10.5$^{f\ 161}$
2,2,2-trichloroethanol							20,$^{e\ 161}$ 13.3$^{f\ 161}$
2-bromoethanol							18,$^{e\ 161}$ 9.5$^{f\ 161}$
2-iodoethanol							18,$^{e\ 161}$ 10.2$^{f\ 161}$
3-chloropropan-1-ol							19,$^{e\ 161}$ 11.1^{f161}
1,1,1,3,3,3-hexafluoropropan-2-ol							18,$^{e\ 161}$ 13.7$^{f\ 161}$

[a] At 20 °C. [b] For $c = 3\%$. [c] From freezing point depression. [d] From MD simulations. [e] Calculated from the accessible surface area. [f] From NMR spectroscopy. [g] From the waveguide dielectric resonance method. [h] From millimeter-wave spectroscopy. [i] From neutron scattering. [j] From X-ray diffraction. [k] From Monte Carlo simulations. [l] From boiling point elevation. [m] From the activity of water calculated from vapor pressure data. [n] From THz TD-ATR spectroscopy. [o] From dielectric relaxation measurements. [p] Per —OH group. [q] From viscosity measurements. [r] At 27 °C.

the assumption of zero compressibility of the solvate is disputable, but any more reasonable assumption of a nonzero value would lead only to a rescaling of the values with the trends conserved.

2.1. Pasynski Method

In 1938, Pasynski presented a method of determining hydration numbers of electrolytes from the speed of sound and density measurements,[11] which was applied by him very shortly thereafter to nonelectrolytic solutes also.[12]

Pasynski assumed, as mentioned above, that the electrostatic field of ions in a solution exerts a very strong static pressure on the surrounding dielectric. As a result, the compressibility of water molecules in the near vicinity of ions (i.e., those located in their hydration sphere) becomes strongly reduced compared with that of pure bulk water or even becomes zero. The effect of such interactions should always be observed as an initial decrease of compressibility of aqueous solutions with increasing concentration, both for electrolytic and for polar nonelectrolytic solutes. It seems true up to now, and is true to the best of our knowledge, that there is no substance reported that initially raises compressibility when added to water.

Let us assume that there is a sample containing n_{H_2O} moles of solvent water of compressibility κ_{S,H_2O}. When n_{solute} moles of a solute are added to it, compressibility of solution falls to $\kappa_{S,solution}$, which was attributed by Pasynski to the $n_h n_{solute}$ moles of solvent (where n_h is the hydration number); this portion of solvent becomes incompressible because of electrostriction of n_h water molecules by one solute molecule. Thus,

$$\frac{\kappa_{S,\,solution}}{\kappa_{S,\,H_2O}} = \frac{n_{H_2O} - n_h n_{solute}}{n_{H_2O}} \tag{2}$$

Simple rearrangement yields the following final formula:

$$n_h = \frac{n_{H_2O}}{n_{solute}}\left(1 - \frac{\kappa_{S,\,solution}}{\kappa_{S,\,H_2O}}\right) \tag{3}$$

The hydration numbers, n_h, of nonelectrolytes calculated from the Pasynski method decrease with increasing concentration and temperature. Of course, as already mentioned, compressibilities of the solute and solvent molecules in the hydration sphere were assumed to be zero.

The dependence $\kappa_{solution} = f(x_{solute})$ for very dilute aqueous solutions of nonelectrolytes ($x_{solute} < 0.01$) can be very satisfactorily approximated by a linear function:[13]

$$\kappa_{S,\,solution} = \frac{d\kappa_{S,\,solution}}{dx_{solute}} x_{solute} + \kappa_{S,\,H_2O} \tag{4}$$

where $d\kappa_{S,solution}/dx_{solute}$ is the slope of the dependence of compressibility on the solute mole fraction. Substitution of eq 4 to eq 3 leads to the following formula for the hydration number in infinitely dilute solutions:

$$n_h^0 = \lim_{n_{solute} \to 0} n_h = -\left(\frac{d\kappa_{S,\,solution}}{dx_{solute}}\right)/\kappa_{S,\,H_2O} \tag{5}$$

The acoustic Pasynski method was often applied to determine the hydration or solvation numbers of simple 1:1, 1:2, 1:3, 2:1,

Table 2. Hydration Numbers of Sugar Alcohols and Carbohydrates at 25 °C^{a}

	method						
			Yasunaga				
solute	Pasynski	Shiio	water + methanol	water + ethanol	water + propan-1-ol	water +2-methyl-propan-2-ol	nonacoustic methods
erythritol			6.6,^{121} 6.0^{122}	3.0^{113,122}	3.0^{122}	2.7^{122}	
pentaerythritol			6.7^{121}				
arabitol			7.4 (D),^{121} 7.3 (D)^{122}	3.9 (D)^{113,122}	4.0 (D)^{122}	4.1 (D)^{122}	
adonitol	7.1^{73,75}						
xylitol	7.39^{b,c26}						2.43,$^{f,g\,172}$ 2.11$^{f,g\,179}$
galactitol	8.4 (D)^{73}		9.1^{121}				
mannitol	8.63 (D),^{b,c26} 8.3 (D)^{73,75}		8.8,^{121} 9.1 (D)^{122}	5.5 (D)^{113,122}	5.5 (D)^{122}	5.2 (D)^{122}	2.00,$^{h\,155}$ 10.8$^{j\,173}$
sorbitol	8.68 (D),^{b,c26} 8.4 (D)^{73}		8.4^{121}				3.31,$^{f,g\,172}$ 3.47$^{f,g\,179}$
inositol	10.62^{b,c26}						
myo-inositol	3.7^{ab69}		10.5^{121}	7.7^{109,113}			67$^{r,ab\ \ 69}$
lactitol							6.98,$^{f,g\,172}$ 7.16$^{f,g\,179}$
maltitol	14.86^{b71}						6.89$^{f,g\,172}$
arabinose	7.83 (D),^{b,c26} 7.72 (L),^{b,c26} 7.6 (D)^{54}	3.5^{101}		4.0 (L)^{109,112,113}			13.0$^{k\,174}$
lyxose	6.8 (D)^{54}			4.1 (D)^{109,113}			13.0$^{k\,174}$
ribose	6.8 (D)^{54}			4.1 (D),^{109,113} 3.9 (D)^{117}			5.7,$^{i,j\,173}$ 12.3,$^{k\,174}$ 2.5 (D),$^{l,m\,175}$ 2.5$^{l,m\,176}$
2-deoxyribose							9.3^{k174}
xylose	7.13 (D),^{b,c26} 6.8 (D)^{54}	2.3^{101}		4.1 (D)^{109,112,113}			12.2,$^{k\,174}$ 1.33$^{n\,177}$
allose							16.1$^{k\,174}$
fructose	9.01 (D),^{b,c26} 8.8 (D)^{54}	3.8^{101}		6.1 (D)^{109,113}			21.9 (D),$^{d,j\,44}$ 2.5 (D),$^{d,o\,44}$ 2.10,$^{h\,155}$ 3.01,^{f,g172} 12.8,^{i,j173} 3.39,^{n177} 3.26 (D),$^{f,g\,178}$ 3.01 (D),$^{f,g\,179}$ 2.93 (D)$^{g\,180}$
galactose	8.91 (D),^{b,c26} 8.7 (D)^{54}			5.2 (D)^{109,113}			16.2,$^{k\,174}$ 1.81,$^{n\,177}$ 3.20 (D),$^{g\,180}$ 16.6,$^{p\,181}$ 24$^{aa\,181}$
2-deoxygalactose							13.0$^{k\,174}$
6-deoxygalactose (fucose)	9.17 (L)^{b,c26}						12.4$^{k\,174}$
glucose	8,^{d12} 8.63 (D),^{b,c26} 6.8 (D),^{d44} 8.4 (D),^{54} 8.48^{b67}	1.4 (D),^{44} 4.3,^{b99} 3.5^{101}		3.5,^{107} 5.2 (D)^{109,112,113}			20.0 (D),$^{d,j\,44}$ 3.2 (D),$^{d,o\,44}$ 2.8,$^{h\,154}$ 2.50−2.51,^{h155} 1.58−1.75,$^{n\,169}$ 3.26,$^{f,g\,172}$ 10.3,$^{i,j\,173}$ 15.8,$^{k\,174}$ 6 (D),$^{l,m\,175}$ 3.7,$^{l,m\,176}$ 1.93,$^{n\,177}$ 3.01 (D),$^{f,g\,178}$ 3.16 (D),$^{f,g\,179}$ 3.26 (D),^{g180} 18.6,^{p181} 24,$^{aa\,181}$ 7.2,$^{p\,182}$ 47.3,$^{q\,183}$ 61.2,$^{r\,183}$ 14.1−15.4 (D),^{l,s184}
2-deoxyglucose				4.0 (D)^{109,113}			12.3$^{k\,174}$
6-deoxyglucose							11.9$^{k\,174}$

Table 2. Continued

	method						
			Yasunaga				
solute	Pasynski	Shiio	water + methanol	water + ethanol	water + propan-1-ol	water +2-methyl-propan-2-ol	nonacoustic methods
3-O-methylglucose	8.1[54]						
mannose	8.35 (D),[b,c26] 8.1 (D)[54]			5.1 (D)[109,112,113]			16.3,[k 174] 3.9[l,m 176]
6-deoxymannose (rhamnose)				3.9 (L)[109,113]			
sorbose	8.91 (L),[b,c26] 9.0 (L)[54]			5.2 (L)[109,113]			
talose	7.7 (D)[54]						16.4[k 174]
cellobiose	14.8[54]	4.8[101]		8.6[109,113]			
gentiobiose	15.6[54]						
lactose	15.87,[b,c26] 15.3[54]			8.2[109,112,113]			6.10,[h 155] 25.1,[i,j 173] 147.6,[q 183] 123[q 185]
lactulose	17.94,[b,c26] 15.2[54]						
maltose	14.27,[b,c26] 14.5,[54] 14.7,[59,64] 14.2,[63] 14.90[b67]	5.3,[b99] 4.2[101]		6.8[109,113]			11.7,[g 63] 5.80,[h 155] 4.1−4.5,[n 169] 24.0,[i,j 173] 5.0,[l,m 176] 4.48,[n 177] 6.93 (D),[g 180] 13,[p,t 186] 10−11,[r 187] 6.50,[u 188] 8.4[v 189]
melibiose	15.5[54]						27.1[p 203]
palatinose	14.75,[b,c26] 14.1[54]						
sucralose	16.42[b,c26]						
sucrose	12−13,[b12] 14.49,[b,c26] 12.3,[d44] 13.9,[54] 14.1,[59,64] 13.8,[63] 14.33[b71]	1.3,[44] 3.8[101]		6.1,[107] 7.0[109,112,113]			22.4,[d,j 44] 7.5,[d,o 44] 11.2,[g 63] 5.0−6.1,[h 154] 4.0,[w 154] 6.00−6.30,[h 155] 3.60−4.83,[n 169] 6.14,[f,g 172,178,179] 25.8,[i,j 173] 6.6,[l,m 176] 3.13,[n 177] 6.59 (D),[g 180] 10,[p,t 186] 6.33,[u 188] 7.5,[v 189] 5.63,[g 190] 11.7,[r,x 191] 7.8−27.5,[r 192] 7.0−37.6,[r 193] 5,[n 194] 7.0−24.7,[r 195] 30[q 196]
trehalose	14.56,[b,c26] 15.3,[54] 12.2,[d55,57,58] 15.2[59,63,64]						12.1,[g63] 5.80,[n 177] 186.4,[q 183] 55.6,[r 183] 12,[p,t 186] 7.95,[u 188] 9.0,[v 189] 7.8−27.5,[r 192,197] 30,[q196] 10,[r 198] 18.9−35.9,[r 199] 16−18,[y,z 200] 25.4[p 203]
turanose	14.2[54]						
maltotriose	21.30[b67]						7.67,[u 188] 34.6[p 203]
melezitose							36.0[p 203]
raffinose	19,[d12] 18.68[b,c26]	6.2[101]					11.90,[h 155] 19.3[i,j 173]
maltotetraose							12.01[u 188]
maltopentaose	34.16[b67]						16.16[u 188]
maltohexaose							20.86[u 188]
maltoheptaose	47.41[b67]						17.01[u 188]
β-D-glucopyranose	7.2[ab69]						89[r,ab 69]
β-D-xylopyranose	6.4[ab69]						70[r,ab 69]

Table 2. Continued

	method						
			Yasunaga				
solute	Pasynski	Shiio	water + methanol	water + ethanol	water + propan-1-ol	water +2-methyl-propan-2-ol	nonacoustic methods
methyl-β-D-arabinopyranoside	8.2[54]			8.2[109,113]			
methyl-α-D-galactopyranoside	9.4[54]						
methyl-β-D-galactopyranoside	9.72,[b,c26] 9.4[54]						
methyl-α-D-glucopyranoside	9.50,[b,c26] 9.2[54]	2.5[101]		7.1[109,113]			
methyl-β-D-glucopyranoside	8.81,[b,c26] 8.8[54]			6.8[109,113]			
methyl-α-D-mannopyranoside	8.9[54]			7.3[109,113]			
methyl-α-D-maltoside							7.0−24.9,[r 201] 4.8−19.1,[r 201] 0.5−17.4[r 201]
methyl-α-D-isomaltoside							7.2−25.5,[r 201] 4.9−20.1,[r 201] 0.6−18.3[r 201]
methyl-β-D-xylopyranoside	7.69,[b,c26] 7.4[54]						
p-nitrophenyl-α-D-galactopyranoside	13.4[64]						
p-nitrophenyl-β-D-galactopyranoside	13.5[64]						
p-nitrophenyl-α-D-glucopyranoside	13.8[64]						
p-nitrophenyl-β-D-glucopyranoside	12.8[64]						
p-nitrophenyl-α-D-mannopyranoside	12.7[64]						
p-nitrophenyl-β-D-mannopyranoside	13.9[64]						
n-octyl-β-D-glucopyranoside	16[56]						
α-cyclodextrin							35,[l 202] 57.5[p 203]
β-cyclodextrin	39.5,[62] 38.0[68]						67.5[p203]
γ-cyclodextrin							48,[l 202] 77.3[p 203]
permethylated α-cyclodextrin							90[l 202]
permethylated β-cyclodextrin							108[l 202]
permethylated γ-cyclodextrin							120[l 202]
β-cyclodextrin with 55% methylated −OH groups							70[l 202]
α-cyclodextrin with 20% 2-hydroxypropylated −OH groups							60[l 202]
β-cyclodextrin with 22% 2-hydroxypropylated −OH groups							70[l202]

Table 2. Continued

	method						
			Yasunaga				
solute	Pasynski	Shiio	water + methanol	water + ethanol	water + propan-1-ol	water +2-methyl-propan-2-ol	nonacoustic methods
γ-cyclodextrin with 22% 2-hydroxypropylated −OH groups							80[l 202]
glucosamine							6.37,[p 181] 24[aa 181]
N-acetylglucosamine							10.4,[p 181] 29[aa 181]
trifluoro-*N*-acetylglucosamine							22.4,[p 181] 34[aa 181]
glucuronic acid							13.0,[p 181] 24[aa 181]
β-D-glucose-6-monophosphate							20.7,[p 181] 32[aa 181]
N-acetylgalactosamine							15.1,[p 181] 29[aa 181]
galacturonic acid							15.6,[p 181] 24[aa 181]
dextran 40000				3.3[e 114]			
dextran 500000				3.0[e 114]			

[a] Enantiomeric form is indicated in parentheses when indicated. [b] At 20 °C. [c] For $c = 3\%$. [d] At 30 °C. [e] Per monomer unit. [f] For $c = 10\%$. [g] From viscosity measurements. [h] From freezing point depression. [i] For $c = 2\%$. [j] From NIR spectroscopy. [k] From volumetric measurements. [l] From dielectric relaxation measurements. [m] At 5 °C. [n] From the activity of water. [o] From conductance. [p] From NMR spectroscopy. [q] From THz spectroscopy. [r] From MD simulation. [s] For $m = 1$ mol·kg^{-1}. [t] For $c = 0.1\%$. [u] From DSC measurements. [v] From neutron scattering. [w] From boiling point elevation. [x] For $c = 6\%$. [y] From depolarized light scattering (DLS) measurements. [z] At 35 °C. [aa] Calculated from the accessible surface area, [ab] At 27 °C.

2:2, 3:1, and 4:1 valence-type electrolytes in aqueous[14−28] and nonaqueous systems[14,29−38] and also in mixed water + organic solvents.[18,19,39−41]

This method was used for determining hydration numbers of polymers, including poly(ethylene glycol)s and poly(vinyl alcohol)s,[42−53] carbohydrates and their derivates,[26,54−69] sweeteners,[70,71] alcohols, glycols, carboxylic acids and amines,[72−77] ethanolamines,[78] amino acids,[73−75,79−81] and albumins of the human serum and hen egg.[82]

There were also attempts to use the Pasynski method to determine the solvation numbers of nonelectrolytic substances in nonaqueous systems, such as polymers in different solvents,[42,45,83−93] acetic acid in methanol,[94] alcohols in olive oil[95] or in propan-1-ol and n-heptane,[96,97] and soybean oil in different organic solvents.[98]

2.2. Shiio Method

Shiio and co-workers developed the method of determination of the hydration numbers from speed of sound and density data.[99−101] On the basis of previous experiments in water−ethanol−solute systems,[99] they assumed that (a) compressibility of the solute molecules can be neglected and (b) water molecules in the hydration spheres have compressibility equal to that of ice, $\kappa_{S,\text{hydration shell}} = 1.8 \times 10^{-10}$ Pa^{-1} (although the source of the latter value was not given). Finally, they derived a formula in the form:

$$\lim_{c\to 0} v_{\text{hydration shell}} = -\frac{1}{c}\left(\frac{\kappa_{S,\text{solution}}}{\kappa_{S,H_2O}} - \frac{\rho_{\text{solution}} - c}{\rho_{H_2O}}\right) \Bigg/ \left(1 - \frac{\kappa_{S,\text{hydration shell}}}{\kappa_{S,H_2O}}\right) \qquad (6)$$

where $v_{\text{hydration shell}}$ is the volume of water bound in hydration shells per gram of solute, $\kappa_{S,\text{solution}}$, and κ_{S,H_2O} are the adiabatic compressibility coefficients of the solution and pure water, respectively, c is the solute concentration expressed as mass per volume, and ρ_{solution} and ρ_{H_2O} are densities of the solution and water, respectively.

Knowing $v_{\text{hydration shell}}$, the hydration number can be calculated from the following equation:

$$n_h = v_{\text{hydration shell}} \frac{M_{\text{solute}}}{V^0_{H_2O}} \qquad (7)$$

where M_{solute} is the molar mass of solute and $V^0_{H_2O}$ is the molar volume of water.

The weakness in this method is the assumption concerning the value of $V^0_{H_2O}$, which is, in fact, unknown for water in the hydration cloud. The same concerns plague the assumption on the value of $\kappa_{S,\text{hydration shell}}$.

The hydration numbers n_h calculated from the Shiio et al. method decrease with increasing concentration and temperature.

Using this method, the hydration numbers of carbohydrates, poly(vinyl alcohol)s, poly(ethylene glycol)s, and other polymers were determined.[44,99−105]

2.3. Yasunaga Method

This method is the only one that exploits the speed of sound and not compressibilities. The advantage of this is that assumptions on solute compressibility and hydration shells are not necessary.

It is well-known that the dependence of the speed of sound versus concentration for aqueous solutions of ethanol (and other nonelectrolytes) is parabolic-like with a maximum located at low nonelectrolyte concentration. If one adds some electrolyte or nonelectrolyte soluble in water to ethanol−water mixed solvent, the maximum of speed of sound shifts toward lower ethanol concentration. Yasunaga and co-workers[106,107] assumed that this is caused only by the solute hydration and that there is no interaction between solute and ethanol (or, better, it is negligible compared with its interaction with water). Therefore, the so-called amount of hydration can be estimated from the following expression:

$$\frac{V_{\text{ethanol}}}{V_{H_2O}} = \frac{V^*_{\text{ethanol}}}{V^*_{H_2O} - V_h} \qquad (8)$$

where V_{ethanol} and V_{H_2O} are, respectively, the volumes of ethanol and water at the maximum of speed of sound in the binary ethanol−water system and V^*_{ethanol}, $V^*_{H_2O}$, and V_h are volumes of ethanol, water, and water bound in hydration shells at the maximum of speed of sound in the ternary ethanol−water−solute system, respectively.

Knowing V_h, the hydration number can be calculated from the following equation:

$$n_h = \frac{\rho_{H_2O} V_h}{n_{\text{solute}} M_{H_2O}} \qquad (9)$$

where ρ_{H_2O} is the density of water, M_{H_2O} is the molar mass of water, and n_{solute} is the number of moles of solute.

This equation was derived on the basis of the hypothesis that the position of the maximum of the speed of sound depends only on the ratio of the amounts of ethanol and free water.

Juszkiewicz employed this method and determined hydration numbers of simple 1:1 and 2:1 valence-type electrolytes,[108,109] tetraalkylammonium halides,[110] poly(ethylene glycol)s,[111] carbohydrates,[112,113] dextran,[114] carboxylic acids, amino acids, peptides,[115,116] amides, nucleosides and nucleotides, nucleic acids,[117−119] polyacrylamides, proteins and caseins,[109] and polyamines.[120]

Antosiewicz and Shugar[121−123] and Juszkiewicz[124−127] modified the Yasunaga method, replacing ethanol with other cosolvents, such as methanol, propan-1-ol, propan-2-ol, 2-methylpropan-2-ol, 1,4-dioxane, acetone, tetrahydrofuran, dimethylformamide, and dimethyl sulfoxide.

The hydration numbers determined using the Yasunaga method increase with increasing temperature and are almost concentration independent. Juszkiewicz also noted[109,127] that in the water−ethanol solvent, the temperature dependences of hydration numbers, n_h^T, at least in the range of temperatures from 5 to 35 °C, is satisfactorily described by the following formula:

$$n_h^T = n_h^{0\,°C} + AT + BT^2 \qquad (10)$$

where $n_h^{0\,°C}$ is the hydration number at 0 °C, T is the temperature in °C, and A and B are the empirical coefficients equal to 0.0383 °C^{-1} and 0.0013 °C^{-2}. This is valid for the majority of investigated nonelectrolytes but only for simple 1:1 valence-type electrolytes. However, this relation is not true for other cosolvents.

Table 3. Hydration Numbers of Polymers at 25 °C

	method			
solute	Pasynski	Shiio	Yasunaga, water + ethanol	nonacoustic methods
di(ethylene glycol)	4.6[73]		5.7[127]	
tri(ethylene glycol)			7.2[127]	
poly(ethylene glycol) 200	10.4,[a][48] 7.4[50]			9.9,[f][50] 0.16[c,f][204]
poly(ethylene glycol) 300				1.14,[c,f][204] 2.06,[c,f][205] 3.4[c,g][206]
poly(ethylene glycol) 400	13.6,[b][44] 21.8,[a][48] 21.0[50]	24.7,[b][44] 22[105]		14.8,[b,h][44] 20.0,[b,i][44] 24.0,[f][50] 2.00,[c,f][204] 2.23,[c,f][205] 3.5[c,g][206]
poly(ethylene glycol) 600	22.5,[b][44] 31,[b][46] 31.8,[a][48] 31.2[50,51]	34.5[b][44]		26.9,[b,h][44] 28.0,[b,i][44] 38.0,[f][50] 2.90,[c,f][204] 2.58[c,f][205]
poly(ethylene glycol) 900				3.44[c,f][205]
poly(ethylene glycol) 1000	50.2,[a][48] 49.1[50]	58[105]		78.9,[f][50] 3.20,[c,f][204] 3.54[c,f][205]
poly(ethylene glycol) 1500	67.0[73]			4.40,[c,f][205] 3.7[c,g][206]
poly(ethylene glycol) 2000	102.9,[a][48] 101.0,[50] 87.0[73]			228.0,[f][50] 5.08,[c,f][205] 136.0[j][207]
poly(ethylene glycol) 3000				6.31,[c,f][205] 3.7[c,g][206]
poly(ethylene glycol) 4000		219[105]		7.73,[c,f][205] 2.4[c,j][208]
poly(ethylene glycol) 6000	1.75[c][42]			10.14[c,f][205]
poly(ethylene glycol) 7500				3.7[c,g][206]
poly(ethylene glycol) 8000				0.9,[j][209] 0.9−1.3[c,j][210]
poly(ethylene glycol) 10000				11.23[c,f][205]
poly(ethylene glycol) 12000				18.98[c,f][205]
poly(ethylene glycol) 15000				18.30[c,f][205]
poly(ethylene glycol) 20000				19.79[c,f][205]
poly(ethylene glycol) 35000				28.44[c,f][205]
poly(ethylene glycol) 43000				2.4[b,k,l][158]
poly(ethylene oxide) 300000	3[c,d][43]			
poly(ethylene oxide) 600000	2.5[b,c][45]			
poly(ethylene oxide) 5000000	3[c,d][43]			
poly(vinyl alcohol)	4.91[c,e][52]			
poly(vinyl alcohol) 1000				2.0−2.2[g,m][171]
poly(vinyl alcohol) 2000				2.0−2.2[g,m][171]
poly(vinyl alcohol) 77000	2.0[a,c][45]			
poly(vinyl alcohol) 110000				3.7−4.0,[m,n][211−213] 3.5[g,m][212]
poly(vinyl alcohol) 125000	1.9[b,c][45]			
polyvinylpyrrolidone	8.54[c,e][52]			
polyacrylic acid	14[c,d][43]			
polyacrylamide	13[c,d][43]			
polyacrylamide 32000			4.1[c][109]	
polyacrylamide 40000			4.1[c][109]	
polyacrylamide 200000			3.7[c][109]	
polyacrylamide 750000	16[b,c][45]			
polyacrylamide 800000				1.9[b,k,l][158]
poly(*N*-isopropylacrylamide) 700000				4.6[b,k,l][158]
guar gum	84[c,d][43]			
xanthan gum	414[c,d][43]			
polyoxyethylene (20) sorbitan monolaurate	28.8[b][44]	60.3[b][44]		114.8[b,h][44]
polyoxyethylene (20) sorbitan monopalmilate	28.2[b][44]	65.8[b][44]		138.0,[b,h][44] 19.0[b,i][44]
polyoxyethylene (20) sorbitan monostearate	25.0[b][44]	63.3[b][44]		158.5,[b,h][44] 22.0[b,i][44]
polyoxyethylene (20) sorbitan monooleate	18.6[b][44]	35.8[b][44]		177.8[b,h][44]

[a] At 20 °C. [b] At 30 °C. [c] Per monomer unit. [d] At 27.8 °C. [e] At 35 °C. [f] From viscosity measurements. [g] From dielectric relaxation measurements. [h] From NIR spectroscopy. [i] From conductance measurements. [j] From DSC measurements. [k] From the waveguide dielectric resonance method. [l] For $c = 10\ \mathrm{g \cdot dm^{-3}}$. [m] Per −OH group. [n] From self-diffusion coefficient of water measurements.

Table 4. Hydration Numbers of Ketones at 25 °C

solute	Pasynski method	Yasunaga method				nonacoustic methods
		water + ethanol	water + propan-1-ol	water + propan-2-one	water +1,4-dioxane	
propan-2-one	2,[a][12] 2.55,[a,b][26] 2.2[73,74]	7.0[127]	8.0[127]	10.7[127]	9.3[127]	1.1[c][214]
butan-2-one	3.5[73,74]	11.7[127]				1.5[c][214]
pentan-2-one	3.9[73,74]					
pentan-3-one	4.2[73,74]					
pentan-2,4-dione	4.0[73]					

[a] At 20 °C. [b] For c = 3%. [c] From FTIR spectroscopy.

Table 5. Hydration Numbers of Carboxylic Acids at 25 °C[a]

solute	method		nonacoustic methods
	Pasynski	Yasunaga, water + ethanol	
formic acid	1.54,[b,c][26] 1.2[73−76,80]		2[d][215]
acetic acid	3,[c][12] 1.8[16,73−76,80]	4.8[109,115,124]	0.00[e][155]
hydroxyacetic acid	2.9[73]	2.7[124]	
trichloroacetic acid	7.27[b,c][26]		
propanoic acid	3,[c][12] 3.23,[b,c][26] 2.7[73−76,80]	8.0[109,115,124]	
lactic acid	3.58[b,c][26]	5.8[124]	0.00[e][155]
2-methylpropanoic acid	3−4[c][12]		
acrylic acid		5.8[109]	
butanoic acid	4,[c][12] 3.5[73−76,80]	9.8[109,115]	
pentanoic acid	3,[c][12] 4.9[73−76]		
oxalic acid	2.9[73−75]		
malonic acid	3.4[73−75]		
succinic acid	4.2[73−75]		
malic acid	11[c][12]		
glutaric acid	4.4[73,75]		
adipic acid	5.7[73,75]		
tartaric acid	14,[c][12] 6.89,[b,c][26] 6.3[73]		2.93−2.94,[e][155] 3.3 (D)[f][169]
citric acid	17,[c][12] 7.52,[b,c][26] 7.4[73]		
gluconic acid	12.52[b,c][26]		
mandelic acid	10−11[c][12]		
quinic acid	8.56[b,c][26]		
gentisic acid	5.0[72]		
gallic acid	6.1[72]		
l-ascorbic acid			5 (L)[g,h][216]
ammonium formate	4.3[28]		
sodium formate	6.9[28,73,76]		9.0[i][217]
ammonium acetate	6.2[28]		
potassium acetate	7.9[28]		
sodium acetate	9.0[28,73,76]	8.0[109]	8.7,[i][218] 4.0,[g,j][219] 3.0−6.1[i,j][220]
sodium propanoate	10.6[28,73,76]		
sodium butanoate	11.6[28,73,76]		
disodium oxalate			15.1[k][221]
disodium malonate			44[k][222]
disodium succinate			23[k][222]

[a] Enantiomer is giving in parentheses when indicated. For comparison a few salts of carboxylic acids are also listed. [b] For *c* = 3%. [c] At 20 °C. [d] From MD simulation. [e] From freezing point depression. [f] From activity of water. [g] From neutron scattering. [h] At 33 °C. [i] From X-ray diffraction. [j] Hydration number of acetate anion. [k] From dielectric relaxation measurements.

Table 6. Hydration Numbers of Amines at 25 °C[a]

	method				
		Yasunaga			
solute	Pasynski	water + ethanol	water + propan-1-ol	water + THF	nonacoustic methods
ammonia	1.1[73−76,80]				1.79−1.85,[b 154] 1.53,[b 155] 7.2[c 223]
hydrazine		1.0[127]			
methylamine	1.7[73−76,80]				2.70,[b 155] 3.0,[c 223] 12,[d 224] 7.1[e 224]
ethylamine	3.2[73−76,80]				3.87,[b 155] 15,[d 224] 11.2[e 224]
ethylenediamine		4.6[120,124,127]	3.1[124]	5.1[124]	16,[d 224] 4.4[e 224]
1-propylamine	3.7[73−76,80]	17.6[124,127]	21.5[124]	20.8[124]	17,[d 224] 14.0[e 224]
2-propylamine	3.9[73,74]				17,[d 224] 15.5[e 224]
1,2-diaminopropane		7.8[124,127]	6.9[124]	8.8[124]	
1,3-diaminopropane		6.5[120,124,127]	5.0[124]	7.1[124]	18,[d 224] 8.6[e 224]
2-methyl-1-propylamine					19,[d 224] 16.1[e 224]
2-methyl-2-propylamine	4.6[73]				18,[d 224] 19.1[e 224]
1-butylamine	4.6[73−76,80]	23.2[127]			19,[d 224] 16.5[e 224]
2-butylamine		21.4[127]			6.0,[f214] 19,[d224] 17.2[e224]
1,4-diaminobutane		9.3[120]			20,[d 224] 11.9[e 224]
1-pentylamine	5.5[73−76,80]				22,[d 224] 12.4[e 224]
1,5-diaminopentane		12.9[120]			23,[d 224] 15.0[e 224]
1,6-diaminohexane		15.2[120]			25,[d224] 22.5[e224]
dimethylamine	2.4[73,75]				4.16[b 155]
diethylamine	4.8[73,75]	20.5[127]			6.10[b 155]
dipropylamine	6.5[73,75]				
triethylamine	6.8[73,75]				6.1[f 214]
bis-(2-aminoethyl)amine		7.4.[120]			
bis-(3-aminopropyl)amine		11.9[120]			
N^1-(2-aminoethyl)-1,3-diaminopropane		9.3[120]			
N^1-(3-aminopropyl)-1,4-diaminobutane		14.0[120]			29,[d 224] 20.8[e 224]
N,*N*′-bis(3-aminopropyl)ethylenediamine		14.7[120]			
N,*N*′-bis(3-aminopropyl)-1,4-butanediamine		21.1[120]			
N^1,$N^{1\prime}$-(butane-1,4-diyl)dipropane-1,3-diamine					38,[d 224] 31.1[e 224]
aniline	4.5[73]				
benzylamine	6.0[73]				
2-amino-2-methylpropane-1,3-diol	5.2[73]				
ethanolamine	2.5[78]				1.50,[b 155] 16,[d 225] 8.4[e 225]
n-propanoloamine					19,[d 225] 13.9[e 225]
n-butanoloamine					21,[d 225] 16.8[e 225]
n-pentanoloamine					23,[d 225] 23.2[e 225]
diethanolamine	4.8[78]				2.55[b 155]
triethanoloamine					2.75[b 155]
methyldiethanolamine	6.0[78]				
dimethylethanolamine	4.3[78]				
ethyldiethanolamine	6.0[78]				
diethylethanolamine	6.3[78]				
2-(dimethylamino)ethanol					3.40[b 155]
2-(2-aminoethoxy)ethanol					4.00[b 155]
4-hydroxypyridine					10.7−11.6[g,h 184]
tris(hydroxymethyl)aminomethane					0.70,[b 155] 14.9−16.6[g,h 184]
trimethylamine-*N*-oxide					27−69,[c 226] 8.5[f 226]
uracil					9[c 227]
1-methyluracil		1.7[109,118]			
methylamine hydrochloride	5.1[28,73,76]				
ethylamine hydrochloride	5.8[28,73,76]				

Table 6. Continued

	method				
		Yasunaga			
solute	Pasynski	water + ethanol	water + propan-1-ol	water + THF	nonacoustic methods
1-propylamine hydrochloride	6.9[28,73,76]				
1-butylamine hydrochloride	7.9[28,73,76]				
1-hexylamine hydrochloride	9.7[28,73,76]				
ethylenediamine dihydrochloride		11.0[120]			
1,3-diaminopropane dihydrochloride		11.0[120]			
1,4-diaminobutane dihydrochloride		11.0[120]			
1,5-diaminopentane dihydrochloride		11.5[120]			
1,6-diaminohexane dihydrochloride		12.5[120]			
bis(2-aminoethyl)amine trihydrochloride		17.0[120]			
N^1-(2-aminoethyl)-1,3-diaminopropane trihydrochloride		17.0[120]			
bis-(3-aminopropyl)amine trihydrochloride		17.0[120]			
N^1-(3-aminopropyl)-1,4-diaminobutane trihydrochloride		18.0[120]			
N,N′-bis(3-aminopropyl)ethylenediamine tetrahydrochloride		23.0[120]			
N,N′-bis(3-aminopropyl)-1,4-butanediamine tetrahydrochloride		23.5[120]			

[a] For comparison a few hydrochlorides of amines are also listed. [b] From freezing point depression. [c] From MD simulations. [d] Calculated from the accessible surface area. [e] From NMR spectroscopy. [f] From FT-IR spectroscopy. [g] From dielectric relaxation measurements. [h] For m = 1 mol·kg^{-1}.

2.4. Isemura and Goto Method

Isemura and Goto derived a formula for the determination of hydration numbers of simple electrolytes,[128] which was then also applied for amino acids and oligopeptides:[129]

$$K = \frac{\kappa_{S,\mathrm{H_2O}} - \kappa_{S,\,\mathrm{solution}}}{c} - \bar{v}\kappa_{S,\mathrm{H_2O}} = -\bar{v}\kappa_{S,\,\mathrm{solute}} + \frac{v_2}{c}(\kappa_{S,\mathrm{H_2O}} - \kappa_{S,\,\mathrm{hydration\ shell}}) \qquad (11)$$

where K is the number of hydration (according to the authors), κ_{S,H_2O}, $\kappa_{S,\mathrm{solution}}$, $\kappa_{S,\mathrm{solute}}$, and $\kappa_{S,\mathrm{hydration\ shell}}$ are the adiabatic compressibility coefficients of the pure water, solution, solute, and water bound in hydration shells, respectively, c is the weight concentration of the solute, $\bar{v}$ is the partial specific volume of the solute given as $\bar{v} = v_1/c$, where v_1 is the volume fraction of the solute, and v_2 is the volume fraction of the water bound in hydration shells. They assumed, similarly to Pasynski, that compressibilites of solute and water molecules in the hydration sphere are equal to zero. We must note, however, that our attempts to reproduce the derivation of Isemura and Goto on the basis of their original papers have been unsuccessful. This may indicate the reason that this method has not been used by anybody (except its authors).

The hydration numbers, n_h, determined using the Isemura and Goto method decrease with increasing concentration and temperature for both electrolytic and nonelectrolytic solutes.

2.5. Millero Method

Millero and co-workers developed a method of determination of hydration numbers, n_h, of electrolytes based on adiabatic partial molar compressibilities at infinite dilution calculated from speed of sound and density data.[130] This method was later also applied to amino acids.[131] They determined n_h using the following formula:

$$n_h = -\frac{\bar{K}^0_{\mathrm{elect}}}{\kappa_{S,\mathrm{H_2O}}V^0_{\mathrm{H_2O}}} \qquad (12)$$

where $\bar{K}^0_{\mathrm{elect}}$ is the electrostriction partial molar compressibility due to hydration and is equal to

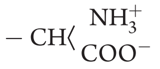
$$\bar{K}^0_{\mathrm{elect}} = \bar{K}^0_{\mathrm{amino\ acid}} - \bar{K}^0_{\mathrm{int}} \qquad (13)$$

$\bar{K}^0_{\mathrm{int}}$ is the intrinsic partial molar compressibility of the amino acid and $\bar{K}^0_{\mathrm{amino\ acid}}$ is the partial molar compressibility of the investigated amino acid in infinite dilution equal to

$$\bar{K}^0_{\mathrm{amino\ acid}} = \lim_{m\to 0} \Phi_{K_S,\,\mathrm{amino\ acid}} = (\kappa_{S,\,\mathrm{solution}}V^0_{\mathrm{solution}} - x_{\mathrm{H_2O}}\kappa_{S,\mathrm{H_2O}}V^0_{\mathrm{H_2O}})/x_{\mathrm{solute}} \qquad (14)$$

where Φ_κ is the adiabatic apparent molar compressibility of the amino acid.

Millero and co-workers calculated hydration numbers for several amino acids assuming $\bar{K}^0_{\mathrm{int}}$ = 0 or $\bar{K}^0_{\mathrm{int}}$ = 3 × 10^{-4} cm^3 mol^{-1} bar^{-1}, the value determined experimentally for a few amides. The average number of water molecules hydrating one molecule of an amino acid was 3.67 ± 0.49 in the former case and 4.04 ± 0.47 in the latter and was related only and strictly to those that are electrostricted in the vicinity of a charged


$-\mathrm{CH}\langle^{\mathrm{NH_3^+}}_{\mathrm{COO^-}}$ group.

Using this method, the hydration numbers of electrolytes[130,132] and amino acids in water and in aqueous solutions containing simple salts[131,133−136] and lysozyme[137,138] were determined.

The hydration numbers n_h for electrolytes determined from the Millero et al. method decrease with increasing temperature.

2.6. Onori Method

Onori assumed[139] that each ion is surrounded by a sphere of water molecules whose density and compressibility are essentially different from those of the bulk water. Furthermore, he assumed that hydrated ions form an ideal solution with the solvent so that the volume additivity rule is valid. If one denotes

Table 7. Hydration Numbers of Amides at 25 °C

		Yasunaga method							
solute	Pasynski method	water + ethanol	water + propan-1-ol	water + THF	water + propan-2-one	water + DMF	water + DMSO	water + propan-2-one	nonacoustic methods
formamide		−0.3[124,126,127]	−1.3[124,126]	−0.5[124,126]	1.6[124,126]	−0.8[124,126]	−1.2[124,126]		1.7[e][228]
N-methylformamide		2.7[124,126,127]	0.8[124,126,127]	2.4[124,126]	4.5[124,126]	1.7[124,126]	1.2[124,126]	4.5[127]	2.8[e][228]
N,*N*-dimethylformamide		5.3[124,126,127]	3.7[124,126,127]	5.4[124,126]	7.4[124,126]	3.8[127]	3.3[124,126]	7.6[127]	2.8[e][228]
N-propylformamide		8.5[124,126,127]							
acetamide		2.8,[109] 2.7[124,126,127]	0.6[124,126,127]	1.9[124,126]	4.0[124,126]	1.8[124,126]	1.3[124,126]	4.0[127]	0.00,[b][155] 14,[c][224] 4.8,[d][224] 2.0[e][228]
N-methylacetamide		5.2[124,126,127]	3.1[124,126]	4.9[124,126]	7.5[124,126]	4.2[124,126]	3.4[124,126]		2.9,[e][228] 31[f][228]
N,*N*-dimethylacetamide		8.2[124,126,127]							2.9[e][214,228]
N-ethylacetamide		8.6[124,126,127]				6.8[124,126]			
thioacetamide		1.6[127]							
N-propylacetamide		10.8[124,126,127]							
propionamide		5.8[109,124,126,127]							17,[c][224] 8.8[d][224]
pentanamide									21,[c][224] 13.6[d][224]
hexanamide									24,[c][224] 18.6[d][224]
acrylamide		4.0[109,124,126,127]							
urea	3−4,[a][12] 2.8[73]	0.1[124,126,127]	−0.6[124,126]	0.0[124,126]	1.6[124,126]	0.3[124,126]	−0.4[124,126]		−0.2,[b][154] 1.1,[g][154] 0.0,[b][155] 2.6−4.2,[h,i][184] 12,[c][224] −0.2,[d][224] 5.0,[e][226] 23−60,[f][226] 6.68,[d][229] 2,[h][230] 2.3−3.2,[h][231] 4.3−7.3,[j][232] −1.5,[k][233] −2.1[k][234]
N-methylurea									12.34,[d][229] 0.4[k][233]
N,*N*-dimethylurea									3.1[k][233]
N,*N*′-dimethylurea									19.79,[d][229] 2.1[k][233]
N,*N*,*N*′,*N*′-tetramethylurea									6.4,[e][214] 7.6[k][233]
N-ethylurea		7.2[124,126,127]							1.5[k][233]
N,*N*-diethylurea		14.8[124,126]							
thiourea		−1.0[127]							

[a] At 20 °C. [b] From freezing point depression. [c] Calculated from the accessible surface area. [d] From NMR spectroscopy. [e] From FT-IR spectroscopy. [f] From MD simulations. [g] From boiling point elevation. [h] From dielectric relaxation measurements. [i] For $m = 1\ \mathrm{mol \cdot kg^{-1}}$. [j] From RISM-SCF method. [k] From millimeter-wave spectroscopy.

Table 8. Hydration Numbers of Nucleosides and Nucleotides at 25 °C

solute	Yasunaga method, water + ethanol
cytidine	2.3,[109] 3.0,[117] 2.3−2.4[118]
thymidine	1.6[109,118]
uridine	2.7,[109] 3.0,[117] 2.6−2.7[118]
deoxyuridine	1.5,[109] 2.0,[117] 1.3−1.8[118]
adenosine 5′-monophosphate sodium salt (5′-AMPNa)	14.0,[109,119] 13.9[117]
adenosine 5′-monophosphate disodium salt (5′-AMPNa$_2$)	21.3[109,119]
cytidine 5′-monophosphate sodium salt (5′-CMPNa)	14.0,[109,119] 13.9[117]
cytidine 2(3′)-monophosphate disodium salt (2(3′)-CMPNa$_2$)	22.2[109,119]
cytidine 5′-monophosphate disodium salt (5′-CMPNa$_2$)	21.2[109,119]
guanosine 5′-monophosphate disodium salt (5′-GMPNa$_2$)	21.5[109,119]
inosine 5′-monophosphate disodium salt (5′-IMPNa$_2$)	22.2[109,119]
uridine 5′-monophosphate disodium salt (5′-UMPNa$_2$)	21.3[109,119]
deoxyribonucleic acid sodium salt (DNANa) DNA = $(C_{39}H_{51}N_{15}O_{25}P_4)_n$	14.3,[109,119] 12.8[117]
deoxyribonucleic acid potassium salt (DNAK) DNA = $(C_{39}H_{51}N_{15}O_{25}P_4)_n$	13.1[109,119]
ribonucleic acid sodium salt (RNANa)	13.9[109,119]
ribonucleic acid potassium salt (RNAK)	12.6[109,119]

the molar fraction of solvent and solute as x_{H_2O} and x_{solute}, respectively, the mean molar volume of solution V^0_{solution} = $(x_{H_2O}M_{H_2O} + x_{\text{solute}}M_{\text{solute}})/\rho_{\text{solution}}$ is given by

$$V^0_{\text{solution}} = (x_{H_2O} - n_h x_{\text{solute}})V^0_{H_2O} + x_{\text{solute}}V^0_h \tag{15}$$

where $V^0_{H_2O}$ is the molar volume of water and V^0_h is the molar volume of hydrated solute. From the pressure derivative under condition of constant entropy and neglecting the pressure dependence of n_h, one obtains

$$\kappa_{S,\text{solution}}V^0_{\text{solution}} = (x_{H_2O} - n_h x_{\text{solute}})\kappa_{S,H_2O}V^0_{H_2O} + x_{\text{solute}}\kappa_{S,h}V^0_h \tag{16}$$

where $\kappa_{S,\text{solution}}$, κ_{S,H_2O} and $\kappa_{S,h}$ are the adiabatic compressibility coefficients of solution, of water, and of hydrated solute, respectively.

From the above equation, one obtains the following expression for molar apparent compressibility $\Phi_{\kappa_{S,\text{solute}}}$ = $(\kappa_{S,\text{solution}}V^0_{\text{solution}} - x_{H_2O}\kappa_{S,H_2O}V^0_{H_2O})/x_{\text{solute}}$:

$$\Phi_{\kappa_{S,\text{solute}}} = -n_h\kappa_{S,H_2O}V^0_{H_2O} + \kappa_{S,h}V^0_h \tag{17}$$

Fitting the linear function $\Phi_{\kappa_{S,\text{solute}}} = -a\kappa_{S,H_2O}V^0_{H_2O} + b$, where $a = n_h$, to the dependence of the molar apparent compressibility on compressibility of water (for different temperatures), where the temperature-dependent argument is $\kappa_{S,H_2O}V^0_{H_2O}$, one can determine hydration number n_h for a given concentration of solute and next extrapolate the obtained values to infinite dilution. It should be noted that this method seems to work well only for medium concentrations. This method, however, yields sometimes irrational values of hydration numbers. For example, Rohman et al. published values of n_h for electrolytes that are higher than the amount of accessible water in the systems.[140−144]

The experimentally determined hydration numbers n_h obtained using the Onori method decrease when concentration increases and are temperature independent. Also the adiabatic compressibility coefficient of the hydrate, $\kappa_{S,h}$, is temperature independent and differs from zero.

Using this method, the hydration numbers for simple 1:1, 1:2, and 2:1 valence-type electrolytes in water[139−151] and in methanol[141−143] and also for amino acids and *N*-acetyl amino acids amides in water[152,153] were determined.

3. TABLES

In this section, the literature data on hydration numbers of nonelectrolytes are collected and presented in Tables 1−9 for different groups of compounds.

Table 10, containing n_h values of globular proteins determined from nonacoustic methods, was added only for illustration and to complete data.

3.1. Alcohols

3.1.1. Pasynski Method. Hydration numbers of alcohols increase linearly with the increase of the alkyl chain length in the homological series. Contribution of $-CH_2-$ group to the total observed hydration number is close to 1.0 for normal alcohols and 1.1 for α,β- and α,γ-diols. On the other hand, elongation of the carbon chain of α,ω-diols results in the increase of the value of n_h of only 0.75 water molecule per $-CH_2-$ group. Hydrogen peroxide fits very well as a first member of the homological series of α,ω-diols. Hydration numbers of the constitutional isomers depend on the positions of the functional groups in the carbon chain. The values of n_h of diols decrease in the order $n_h^{\alpha,\beta\text{-diol}} > n_h^{\alpha,\gamma\text{-diol}} > n_h^{\alpha,\omega\text{-diol}}$. Shift of the $-OH$ group from the β position in α,β-diols to the γ position in α,γ-diols reduces the values of the n_h by ca. 0.6.

3.1.2. Yasunaga Method. Hydration numbers of alcohols determined by the Yasunaga method also increase linearly with the alkyl chain length in the homological series but depend on the cosolvent used in the experiment: 5.8 (in water−methanol), 6.8 (in water−ethanol), 8.9 (in water−THF), 11.7 (in water−2-methylpropan-2-ol), and 11.9 (in water−propan-1-ol system) water molecules fall to one $-CH_2-$ group in the homological series of normal alcohols. This raises some doubts about the foundations of this method.

3.2. Polyols and Carbohydrates

3.2.1. Pasynski Method. Hydration numbers of sugar alcohols increase linearly with the increase of the molecule chain

Table 9. Hydration Numbers of Amino Acids and Their Derivates at 25 °C[a]

solute	method					nonacoustic methods
	Pasynski	Yasunaga, water + ethanol	Isemura and Goto	Onori	Millero	
alanine	5,^{b12} 6.2 (L)$^{73-75,80,81}$	7.8^{109,115,116}	3.35^{b128}	19.6^{152}	3.16 (D),^{131} 3.57 (D),^{131} 3.16 (L),^{131} 3.57 (L),^{131} 3.09 (DL),^{131} 3.51 (DL),^{131} 2.89 (DL),^{133} 3.17 (DL),^{134} 3.48 (L),^{135} 3.06 (L),^{135} 3.41 (L)^{136}	3.41 (D),$^{d\,131}$ 3.94 (D),$^{d\,131}$ 3.41 (L),$^{d\,131}$ 3.94 (L),$^{d\,131}$ 3.41 (DL),$^{d\,131,235}$ 3.94 (DL),$^{d\,131}$ 2.21 (DL),$^{e\,134}$ 4.66 (L),$^{d\,135}$ 3.43 (L),$^{d\,135}$ 4.65 (DL),$^{d\,235}$ 2.6 (DL),$^{f\,236}$ 3.3 (L),$^{f\,236}$ 3.49 (DL),$^{d\,237}$ 3.8,$^{d\,238}$ 1.75 (L),$^{g\,239}$ 15,$^{h,i\,240}$ 15.1 (L)$^{h,i\,241,242}$ 7 (L)^{r243}
arginine		6.9 (L)^{116}			3.29 (L),^{131} 3.66 (L)^{131}	5.40 (L),$^{d\,131}$ 3.94 (L),$^{d\,131}$ 17,$^{h,i\,240}$ 19.6,$^{h,i\,241}$ 7.5$^{d,j\,244}$
asparagine		4.3 (D)^{116}	3.07^{b128}			6.1 (L),$^{f\,236}$ 11,$^{h,i\,240}$ 10.8,$^{h,i\,241}$ 5.6,$^{d,j\,244}$ 11.9$^{k\,245}$
aspartic acid			3.80^{b128}		4.09 (DL),^{131} 4.46 (DL)^{131}	4.85 (DL),$^{d\,131}$ 3.94 (DL),$^{d\,131}$ 13,$^{h,i\,240}$ 13.1,$^{h,i\,241}$ 5.0,$^{d,j\,244}$ 8−10$^{k\,246}$
cysteine					4.06 (L),^{131} 4.43 (L)^{131}	4.95 (L),$^{d\,131}$ 3.94 (L),$^{d\,131}$ 1.7$^{d,j\,244}$
glutamic acid	7.9 (DL)^{73}		4.11^{b128}		4.48,^{131} 4.84^{131}	5.41,$^{d\,131}$ 3.94,$^{d\,131}$ 13,$^{h,i\,240}$ 13.3,$^{h,i\,241}$ 5.0$^{d,j\,244}$
glutamine			4.13^{b128}			0.00,$^{l\,155}$ 13.3 (L),$^{f\,236}$ 15,$^{h,i\,240}$ 15.0,$^{h,i\,241}$ 5.4$^{d,j\,244}$
glycine	5,^{b12} 5.5$^{73-75,80,81}$	4.4,^{107} 5.7^{109,115,116}	3.40^{b128}	12.8^{152}	3.34,^{131} 3.67,^{131} 3.26,^{133} 3.34,^{134} 3.56,^{135} 3.23^{135}	3.97,$^{d\,131}$ 2.63,$^{d\,131,135,235}$ 0.78,$^{e\,134}$ 3.52,$^{d\,135}$ 0.00,$^{l\,155}$ 11.4,$^{d\,174}$ 3.52,$^{d\,235}$ 8.2,$^{f\,236}$ 2.72,$^{d\,237}$ 2.9,$^{d\,238}$ 3.7,$^{h,i\,240,241}$ 3.8,$^{h,i\,242}$ 8.4,$^{k\,245}$ 7,$^{m\,247}$ 2.2,$^{f,n\,248}$ 4.2,$^{o\,249}$ −2.0 to −1.2$^{h\,250}$
histidine			4.62^{b128}		3.94,^{131} 4.29^{131}	6.83,$^{d\,131}$ 3.27,$^{d\,131}$ 35.6 (L),$^{f\,236}$ 15,$^{h,i\,240}$ 14.9,$^{h,i\,241}$ 4.2,$^{d,j\,244}$ 10.2$^{k\,245}$
isoleucine	9.8 (L)^{73,80,81}			38.5 (L)^{152}		24.0 (L),$^{f\,236}$ 8.60 (L),$^{g\,239}$ 37,$^{h,i\,240}$ 37.4 (L)$^{h,i\,241,242}$
leucine	9.5 (D),^{73} 9.7 (L)$^{73-75,80,81}$		4.53^{b128}	41.1 (L)^{152}	3.93 (L),^{131} 4.30 (L),^{131} 3.87 (L)^{134}	3.94 (L),$^{d\,131}$ 4.96 (L),$^{d\,131,235}$ 6.79 (L),$^{e\,134}$ 7.09 (L),$^{d\,235}$ 13.9 (DL),$^{f\,236}$ 8.3 (L),$^{f\,236}$ 5.5,$^{d\,238}$ 8.53 (L),$^{g\,239}$ 34,$^{h,i\,240}$ 33.7 (L)$^{h,i\,241,242}$
lysine	10.5 (L)^{73,81}	12.8 (DL)^{109,115,116}				20.1 (L),$^{f\,236}$ 20,$^{h,i\,240}$ 19.4,$^{h,i\,241}$ 2.8$^{d,j\,244}$
methionine			4.53^{b128}	38.6 (DL)^{152}	3.85 (DL),^{131} 4.22 (DL)^{131}	6.16 (DL),$^{d\,131}$ 3.94 (DL),$^{d\,131}$ 21.1 (L),$^{f\,236}$ 6.17 (DL),$^{d\,237}$ 22,$^{h,i\,240}$ 21.6,$^{h,i\,241}$ 1.8$^{d,j\,244}$
phenylalanine	10.6 (L)^{73,81}	14.1 (DL)^{116}	4.48^{b128}	46.9 (L)^{152}	4.28,^{131} 4.64^{131}	5.22,$^{d\,131}$ 4.15,$^{d\,131}$ 4.94 (DL),$^{d\,237}$ 7.51 (L),$^{g\,239}$ 31,$^{h,i\,240}$ 30.9$^{h,i\,241}$
proline	7.58 (L)^{b,c26}	7.9 (DL)^{109,115,116}	3.26^{b128}	27.1 (L)^{152}	2.87 (L),^{131} 3.24 (L)^{131}	2.89 (L),$^{d\,131}$ 4.18 (L),$^{d\,131}$ 29.9 (L),$^{f\,236}$ 16,$^{h,i\,240}$ 15.6,$^{h,i\,241}$ 2.9$^{f,n\,248}$
serine	6.9 (DL)^{73,81}	6.9 (DL)^{116}	4.04^{b128}			4.2 (DL),$^{f\,236}$ 3.91 (L),$^{d\,237}$ 11,$^{h,i\,240}$ 10.6,$^{h,i\,241}$ 3.1,$^{d,j\,244}$ 10.2$^{k\,245}$
threonine			4.06^{b128}			3.38 (L),$^{d\,237}$ 16,$^{h,i\,240}$ 16.2,$^{h,i\,241}$ 3.1,$^{d,j\,244}$ 10.0$^{k\,245}$
tryptophan				46.0 (L)^{152}	3.72 (D),^{131} 4.11 (D)^{131}	8.83 (D),$^{d\,131}$ 4.58 (D),$^{d\,131}$ 22.0 (L),$^{f\,236}$ 33,$^{h,i\,240}$ 32.7,$^{h,i\,241}$ 1.6^{d,j244}
tyrosine						27.0,$^{h,i\,240,241}$ 2.5,$^{d,j\,244}$ 10.6$^{k\,245}$

Table 9. Continued

solute	method					nonacoustic methods
	Pasynski	Yasunaga, water + ethanol	Isemura and Goto	Onori	Millero	
valine	8.5 (L)[73,75,80,81]	13.6 (DL)[109,115,116]	4.22[b128]	30.6 (L)[152]	3.78 (L),[131] 4.16 (L),[131] 3.71 (L),[134] 3.92 (L),[135] 3.54 (L)[135]	3.94 (L),[d131] 3.43 (L),[d131,235] 4.34 (L),[e134] 5.15 (L),[d135] 3.40 (L),[d135] 5.18 (L),[d235] 4.9 (DL),[f236] 3.21 (DL),[d237] 3.9,[d238] 7.37 (L),[g239] 30,[h,i240] 30.2 (L)[h,i241,242]
N-methylglycine (sarcosine)	6.0[73]					2.8[f,n248]
N,*N*-dimethylglycine						2.7[f,n 248]
N,*N*,*N*-trimethylglycine (betaine)						9,[o230] 2.9[f,n 248]
hydroxyproline						16.2 (L)[f 236]
ectoine						3.8[f,n 248]
hydroxyectoine						3.6[f,n 248]
3-aminopropanoic acid (β-alanine)		6.8[109,115]				4.10,[d 237] 2.8[f,n 248]
2-aminobutanoic acid		9.9 (DL)[109,115,116]			3.16 (DL)[134]	2.99 (DL),[e 134] 6.80 (DL)[g 239]
4-aminobutanoic acid	7.2[73,80]					10.3−11.3,[o,p 184] 3.3,[f,n 248] 6.5−8.5[k251]
2-aminopentanoic acid (norvaline)						10.61 (DL)[g 239]
5-aminopentanoic acid						3.7[f,n 248]
2,5-diaminopentanoic acid (ornithine)		11.0 (DL)[116]				
2-aminohexanoic acid (norleucine)						11.80 (DL)[g 239]
6-aminohexanoic acid	10.0[73]					14.6−17.3,[o,p 184] 3.9[f,n 248]
diglycine		8.9[109,115,116]	4.70[b128]			5.67,[d 252,253] 5.69,[d 254] 5.70[d 255]
triglycine		12.8[109,115,116]	5.66[b128]			10.5−13.0[o,q 184]
tetraglycine			6.38[b128]			
glycyl-L-alanine		11.0[109,115,116]				
glycyl-L-asparagine		6.8[116]				
glycyl-L-leucine		20.0[109,116]				11.22[d 254]
glycyl-L-methionine		14.0[116]				
glycyl-L-proline		10.7[109,115,116]				
glycyl-L-tyrosine		11.0[116]				
glycyl-L-valine		17.6[109,115,116]				9.54[d 254]
L-alanylglycine		10.8[109,115,116]				
DL-alanyl-DL-alanine		12.8[109,115,116]				
DL-leucylglycine		20.0[109,116]				
glycyl-DL-alanylglycine		13.5[109,115,116]				
D-leucylglycylglycine		25.0[116]				

Table 9. Continued

	method					
solute	Pasynski	Yasunaga, water + ethanol	Isemura and Goto	Onori	Millero	nonacoustic methods
Tyr-Gly-Phe-Ala-Obz (Tyr-Gly-Phe-Ala-*O*-benzyl ester)						6.4$^{d\,256}$
(L-prolyl-L-prolylglycyl)$_5$						130−135$^{o\,257,258}$
(L-prolyl-L-prolylglycyl)$_{10}$						250−270$^{o\,259}$
alanine hydrochloride	7.0 (L)^{81}					
arginine monohydrochloride		8.6 (L)^{116}				
asparagine hydrochloride		5.4 (D)^{116}				
glycine hydrochloride	6.7^{81}					5$^{m\,247}$
histidine monohydrochloride		6.5 (L)^{116}				
isoleucine hydrochloride	9.5 (L)^{81}	15.4 (L)^{116}				
leucine hydrochloride	10.1 (L)^{81}	17.2 (L)^{116}				
lysine monohydrochloride		13.6 (L)^{116}				
lysine dihydrochloride	13.1 (L)^{81}					
methionine hydrochloride		11.7 (DL)^{116}				
phenylalanine hydrochloride	11.4 (L)^{81}	15.5 (DL)^{116}				
serine hydrochloride	7.9 (L)^{81}					
tryptophan monohydrochloride		11.2 (DL)^{116}				
valine hydrochloride	8.7 (L)^{81}					
ornithine monohydrochloride		12.2 (DL)^{116}				
4-aminobenzoic acid 2-diethylaminoethyl ester hydrochloride (Procaine hydrochloride)	13.9^{62}					
alanine sodium salt	10.6 (L)^{81}					
glycine sodium salt	9.4 (L)^{81}					10$^{m\,247}$
isoleucine sodium salt	14.5 (L)^{81}					
leucine sodium salt	14.2 (L)^{81}					
lysine sodium salt	13.6 (L)^{81}					
phenylalanine sodium salt	15.2 (L)^{81}					
serine sodium salt	10.9 (L)^{81}					
valine sodium salt	13.7 (L)^{81}					
N-acetyl-glycine amide				23.67^{153}		
N-acetyl-alanine amide				27.89^{153}		
N-acetyl-valine amide				39.54^{153}		
N-acetyl-leucine amide				58.23^{153}		
N-acetyl-lysine						4.0^{f,n248}

[a] Stereoisomers when indicated are provided in parentheses. For comparison a few salts of amino acids are also listed. [b] At 20 °C. [c] For c = 3%. [d] From volumetric measurements. [e] From viscosity measurements. [f] From NIR spectroscopy. [g] From microwave dielectric method. [h] From millimeter-wave spectroscopy. [i] At 30 °C. [j] Hydration numbers of amino acid side chains. [k] From Monte Carlo simulations. [l] From freezing point depression. [m] From DSC measurements. [n] For m = 2 mol·kg^{-1}. [o] From dielectric relaxation measurements. [p] For m = 1 mol·kg^{-1}. [q] For m = 0.25 mol·kg^{-1}. [r] From MD simulations.

Table 10. Hydration Numbers of Globular Proteins at 25 °C

solute	nonacoustic methods
hemoglobin	3822 (2834)[a,b] [174]
ovalbumin	2972 (1882)[a,b] [174]
pepsin	2994 (1524)[a,b] [174]
α-chymotrypsinogen A	2825 (1202)[a,b] [174]
α-chymotrypsin	2756 (1184)[a,b] [174]
trypsin	2599 (1056)[a,b] [174]
trypsinogen	2367 (1075)[a,b] [174]
myoglobin	1692 (857)[a,b] [174]
α-lactalbumin	1801 (802)[a,b] [174]
lysozyme	233,[a] [138] 1814 (752),[a,b] [174] 710−720,[c] [260] 503,[c] [261] 625−672[c,d] [261]
ribonuclease A	1835 (754)[a,b] [174]
cytochrome *c*	1114 (679)[a,b] [174]

[a] From volumetric measurements. [b] The number of water molecules within the first hydration shell of each protein is shown in parentheses. [c] From MD simulations. [d] In unfolded conformation.

length $H(CHOH)_{n+1}H$. Approximately 1.5 water molecules are hydrating one >CHOH group. Methanol and ethane-1,2-diol fit very well as the two first members of the homological series of polyols.

The average hydration numbers of aldopentoses, aldohexoses, and ketohexoses are ca. 7.0, 8.2, and 8.9, respectively. Methylation and *p*-nitrophenylation of the glycosidic oxygen atom at the anomeric center increase the hydration number of monosaccharide by about 0.6 and 5.0 water molecules, respectively. Hydration numbers of di- and oligosaccharides are lower than the sum of the hydration numbers of constituent monosaccharides by 1.7 to 3.6 water molecules per each glycosidic bond.

3.2.2. Shiio Method. The average hydration number of monosaccharides is around 3.4. Hydration numbers of disaccharides are almost the same as the hydration numbers of single monosaccharides.

3.2.3. Yasunaga Method. The average hydration numbers of aldopentoses, aldohexoses, and ketohexoses in water−ethanol solutions are ca. 4.1, 5.2, and 5.7, respectively. Methylation of the glycosidic oxygen atom at the anomeric center increases the hydration number of monosaccharide by 2.0−4.2 water molecules. Hydration numbers of disaccharides are lower for about 2.2−4.3 water molecules then the sum of hydration numbers of constituent monosaccharides; 3.0−3.3 water molecules fall to one monomer unit in dextran solutions.

3.3. Polymers

3.3.1. Pasynski Method. Hydration numbers of poly(ethylene glycol)s increase linearly with the increase of their polymerization degree. Depending on temperature, 2−3 water molecules fall to one $-CH_2CH_2O-$ monomer unit.

3.3.2. Shiio Method. Hydration numbers of PEG increase linearly with the polymer chain length. The contribution of an ethylene oxide unit to the total observed n_h for PEG polymers is about 2.4, which is similar to that from the Pasynski method.

3.3.3. Yasunaga Method. The hydration number of an $-CH_2CHCONH_2-$ group in poly(acryl amide)s is almost independent of polymer molar mass and equal to ca. 3.7−4.1 water molecule per monomer unit.

3.4. Carboxylic Acids

3.4.1. Pasynski Method. Hydration numbers of mono- and α,ω-dicarboxylic acids increase linearly with increase of the carbon chain length in the homological series. Contribution of $-CH_2-$ group to the total observed hydration number is 0.9 for monocarboxylic acids and 0.7 for α,ω-dicarboxylic acids. About 1.0 and 1.4 water molecules fall to one −COOH group for mono- and dicarboxylic acids, respectively.

3.4.2. Yasunaga Method. Approximately 2.5 water molecules are hydrated to one methylene group in the homological series of monocarboxylic acids in water−ethanol system.

3.5. Amines

3.5.1. Pasynski Method. Hydration numbers of primary, secondary, and tertiary amines increase linearly with increase of the alkyl chain length in homological series. The n_h's also increase linearly with the degree of substitution of ammonia hydrogen atoms with $-C_nH_{2n+1}$ and $-C_nH_{2n}OH$ groups. Ammonia fits very well as a first member of the homological series of primary, secondary, and tertiary alkyl amines and amino alcohols. For primary, secondary, and tertiary alkyl amines and primary amines hydrochlorides, the proportion of water falls to 0.9 molecules per methylene group.

Contribution of the ammonia group $-NH_2$ to the total n_h of an amine molecule is ca. 1.1 and increases with the degree of substitution: $n_h^{-NH_2} < n_h^{=NH} < n_h^{\equiv N}$.

3.5.2. Yasunaga Method. Hydration numbers of α,ω-diamines increase linearly with the increase of the alkyl chain length in the homological series. Contribution of each $-CH_2-$ group to the total observed hydration number is 2.7. Hydration numbers of α,ω-diamines are ca. 2.5 times lower than for respective normal amines. Hydration numbers of hydrochlorides of polyamines derived from Yasunaga method do not depend on the alkyl chain length and are equal to ca. 11.0, 17.0, and 23.0 for diamine dihydrochlorides, triamine trihydrochlorides, and tetraamine tetrahydrochlorides, respectively.

3.6. Amides

3.6.1. Yasunaga Method. Hydration numbers of amides and ureas determined by the Yasunaga method depend on the cosolvent used in the experiment. Hydration numbers of amides increase linearly with increase of the carbon chain length in both acyl and amine groups. The n_h's of amides and ureas also linearly increase with the degree of substitution of ammonia hydrogen atoms by alkyl $-C_nH_{2n+1}$ groups. However, the values of n_h of formamide, urea, and thiourea determined by this method are negative.

3.7. Amino Acids

3.7.1. Pasynski, Yasunaga, and Onori Methods. Hydration numbers of amino acids increase with increase of the length of the solute molecules but depend also on the type and number of the functional groups that are their constituents. The values of n_h of an amino acid increase in the direction: $n_h^{\text{Pasynski method}} < n_h^{\text{Yasunaga method}} < n_h^{\text{Onori method}}$.

3.7.2. Isemura and Goto and Millero Methods. The average number of water molecules hydrating one molecule of an amino acid is 4.0 ± 0.5 and 3.9 ± 0.5 by the Isemura and Goto and the Millero methods, respectively. However, according to the Millero method, this number is related only and strictly to those water molecules that are electrostricted in the vicinity of a charged

$-CH\langle{}^{NH_3^+}_{COO^-}$ group.

4. CONCLUSIONS

It is not the intention of this paper to criticize some methods or to prefer others. However, a general evaluation can be made, at least on the basis of reliability of assumptions or the final results generated by different algorithms and models.

(1) The hydration numbers determined from Yasunaga method increase with increasing temperature and are almost concentration independent. It is obvious that the results should behave contrariwise. Moreover, Yasunaga assumed that there is no interaction between solute and cosolvent (it is negligible compared with interaction with water), an assumption that seems rather risky. Last but not least, one could also note that applying this method is extraordinarily time- and labor-consuming.

(2) The assumptions of the Shiio attempt are numerous but also risky: (a) zero compressibility of the solute; (b) the compressibility of hydration shell equal to that of ice (but the value used by Shiio, 1.8×10^{-10} Pa^{-1}, is not documented); (c) the molar volume of water in the hydration sphere equal to that of pure water. However, the resulting n_h's seem to be reliable, although they are low compared with other methods.

(3) The hydration numbers obtained by the Onori method are temperature independent, rather than what is expected. In this model, the adiabatic compressibility coefficient of the hydrated solute $\kappa_{S,h}$ is equal to that of solution at the concentration where $\kappa_{S,\mathrm{solution}}$ is independent of temperature. Moreover, it varies with the type and strength of solute−water interactions. Other assumptions of the Onori method are reliable, and thus it is worthy of interest. However, the resulting values of the hydration numbers of some electrolytes happen to be irrationally high, exceeding the amount of water existing in the system.

(4) It is interesting that the assumptions of the Isemura−Goto method are similar to those of Pasynski, and one would expect that the results of these two methods would also be identical. So far, however, such a comparison has not been done.

(5) The Millero method was derived for amino acids and is hardly applicable for any wider range of systems. Moreover, it assumes a nonzero compressibility of hydrates (or, more precisely, the hydrated parts of amino acid molecule), and the value of this quantity is the subject of supposition, not experiment. There are no data on the concentration dependence of the hydration numbers determined by this method.

(6) Hydration numbers of nonelectrolytes calculated using the Pasynski method decrease with increasing concentration and temperature, as expected. The weakness of the Pasynski attempt is assuming rather nonrealistic compressibility of hydrate, $\kappa_{S,h}$, equal to zero. On the other hand, one could assume any nonzero value of $\kappa_{S,h}$ (that of ice, 1.2×10^{-10} Pa^{-1},[262] or that of solid crystalline hydrates, 4.0×10^{-10} Pa^{-1},[263] could be interesting alternatives): in that case the values of n_h obtained will be higher, but all the trends should be conserved.

The differences between hydration numbers obtained by different acoustic methods result from different assumptions. The basic problem is not only the compressibility of hydrate itself (Pasynski, Onori) or the solute molecule (Shiio, Isemura−Goto, Millero) or the hydration shell (Shiio, Isemura−Goto), but also the choice of function describing the dependence of compressibility on composition of the solution (Shiio, Isemura−Goto).

Molecular interpretation of the data on hydration numbers is difficult. Chalikian[174] assumed that water in the hydration shell is a mixture of two states and found the differences in proportions between them depending on the type of hydrated group (charged, polar, or nonpolar). The idea of "anchoring" of the polar groups, which are able to form hydrogen bonds with water, and simultaneous hydrophobic-type hydration of the nonpolar tails of the solute molecule is also often exploited.[109] It was shown that the hydration numbers are nicely additive with the constituents of the solute molecule, if, of course, one consistently applies the same method of determining n_h's.[75,109,174] This is an additional argument for building a systematic database of the hydration numbers for a wide variety of compounds, in particular for homologic series of solutes. So, independent of their simplified assumptions, the acoustic methods are preferred because of their simplicity and also their applicability to very dilute systems.

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