

VOLUMETRIC PROPERTIES OF AQUEOUS SOLUTIONS
OF POLAR NON-IONIC COMPOUNDS

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Introduction

The non-electrolyte solutions can, under the point of view of their interaction with water, be classified into two groups: a first one is made up of non-polar compounds (e.g. saturated hydrocarbons) and a second one of compounds where polar groups such as -OH, -O-, >C=O , -NH_2 , -CONH_2 , >S=O predominate.

The action of non-polar solutes on the structure of water, in general terms, can be taken as known. This action is believed to intensify the own structure of the solvent in its neighbourhood and is called hydrophobic hydration⁽¹⁻⁴⁾.

The polar groups, attending to their capacity of behaving as proton donors or acceptors, form hydrogen bonds with water. This type of interaction is known as hydrophilic hydration⁽⁵⁾.

Once the polar groups have a spacial orientation, the bonds formed between these groups and the water are also oriented. From this feature two important consequences result: the first is the possibility of solute-solvent interaction to disturb the structure of the water beyond the molecular layer of the solvent in contact with the solute, once the orientation of the hydrogen bond most likely is not compatible with the tetrahedral water structure. The second is the dependence of the hydration on the conformation of the solute molecule. For instance, it is believed

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that an hydroxyl group bound to a monosaccharide ring interact with the water differently whether it is in equatorial or axial position (5,6,7).

Given the type of structure resulting from the addition of a non-polar solute to the water, the solutions thus obtained are called aqueous, whereas the polar solute give rise to normal solutions. The two types of interaction, hydrophobic and hydrophilic, have different translation in the thermodynamic properties.

Table 1 shows data for some thermodynamic excess functions and for the partial molar heat capacity of aqueous and normal solutions.

Table 1.- Classification of binary aqueous mixtures according to thermodynamic functions

Classification	Thermodynamic functions	Examples
Typically aqueous solutions	$G^E > 0$ $ T S^E > H^E $ $C_{p,2}^0$ high	Monoalcohols, cetones, tetrahydrofuran, dioxan
Typically nonaqueous solutions	$G^E > 0$ $ H^E > T S^E $ $G^E < 0$ $ H^E > T S^E $	Acetonitril, propylene carbonate Hydrogen peroxide, dimethylsulfoxide

So far we have referred the behaviour of polar and non-polar groups but we must have in mind that, generally, solutes have simultaneous both of groups having therefore a mixed behaviour. When the polar part predominates their features get closer to those of typically aqueous systems. On the other side, if the polar part is the predominant one, then they form normal solutions.

As a consequence, though we have chosen for this lecture the hydration of polar compounds we cannot fail to consider solutes in a wider range of polarity. We will try to give an idea of the state of knowledge on their hydration, presenting the P-V-T results.

Hydration and conformation of the solute

It has been admitted that a polar group interacts more strongly with water when its position and orientation adapts itself to an ice-like water structure.

Warner⁽⁸⁾ has admitted that the conformation of polypeptides in aqueous media is such that the carbonyl groups were disposed in hexagonal ring arrangements. In this conformation the oxygen atoms of each peptide unit coincides with the oxygen second neighbours of the water at nearly the human physiological temperature. So the forces towards water are intensified and the structure of this solvent is not strongly disturbed. In the same line of thought it has been accepted that even in molecules of rigid structure, the interaction forces with water are strongly dependent on the structure of water itself. It is the case, for example, of monosaccharides which exhibit different values for thermodynamic properties depending on the ratio between the number of hydroxyl groups in equatorial and axial position.

The distance between the oxygen of neighbour hydroxyl groups bound to the ring, is nearly the same as that of the oxygen neighbours in water. However, due to the orientation of the O-H bonds, if the group is equatorial the hydrogen bonds formed with water are compatible with the tetrahedral structure of water. This is not the case for an axial group. Thus the different conformers of pentoses or hexoses have different hydration energies. Fig. 1 shows the O-O spacing in ice lattice, and in a monosaccharide, and the perturbation produced in water by adding a monosaccharide molecule

with all hydroxyl groups equatorially oriented (β -glucose), or a molecule (hypothetic) with all groups axially oriented.

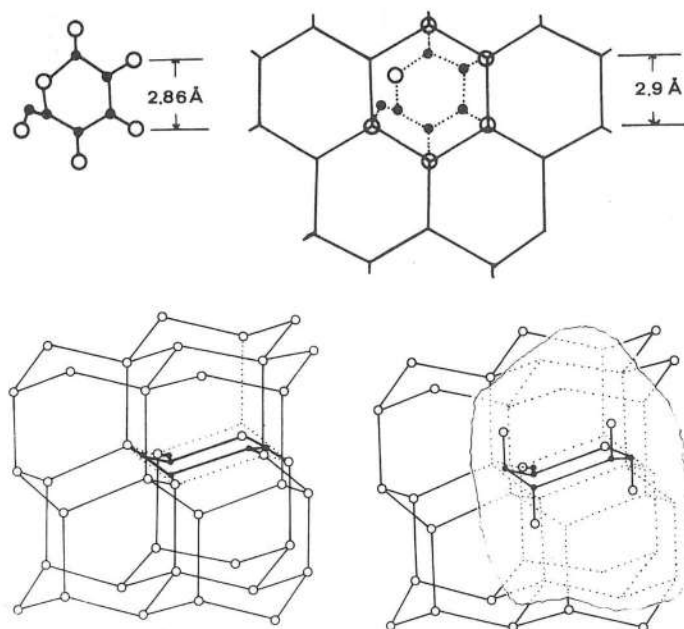


Fig. 1.- Disruption of the ice-like water structure by a monosaccharide molecule

Apparent molar volume

The molar volume of a solution obtained by dissolving n_2 solute molecules and n_1 solvent molecules is given by

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2 \quad (1)$$

\bar{V}_1 and \bar{V}_2 are the partial molar volumes of components 1 and 2. Introducing the apparent molar volume, equation (1) is written as

$$V = n_1 \bar{V}_1^0 + n_2 \phi_V \quad (2)$$

Comparing equation 1 and 2 at infinite dilution we have $\phi_V^0 = \bar{V}_2^0$

ϕ_V can be calculated from water and solution densities by the well known equation

$$\phi_V = \frac{1000(d_1 - d)}{m d d_1} + \frac{M_2}{d} \quad (3)$$

d and d_1 are the densities of solution and water respectively, m is the molarity and M_2 the solute molecular weight.

As density can be measured with high precision with a simple technique, the limiting value of the partial molar volume of the solute can, therefore, be accurately determined. (26)

Values for \bar{V}_2^0 are given in literature for a large number compounds. Table II shows those values for some common compounds.

The apparent molar volume can be considered as a sum of two terms: one corresponding to a cavity for introducing the solute molecule, and the other due to the variation of the volume resulting from solute-solvent interaction

$$\bar{V}_2^0 = \bar{V}_S^0 + \bar{V}_i^0 \quad (4)$$

The main problem in using eq (4) is the fact that we cannot determine \bar{V}_S^0 with sufficient accuracy. However, some conclusions have been drawn from the volume data.

Plotting ϕ_V^0 vs van der Waals volumes of compounds with different polarities, Terasawa et al (22) showed the relative effects of the polar and non-polar parts of the solute on the volume. It is observed that the decreasing in volume produced by the non-polar part is much smaller than that due to the polar one. A figure around 4.5 cm^3 per mole has been assigned to the hydrogen bond produced by the hydroxyl group.

Another attempt worth noting was worked out by Farrell et al. (16,21,23) trying to reproduce the experimental data obtained for the apparent molar

volume of mono- and oligo-saccharides using the following equation

$$\phi_V^O = \frac{4}{3} \pi N(r_W + \Delta)^3 - n\sigma \quad (5)$$

N is the Avogadro number, r_W is the van der Waals radius, Δ is the increasing of the radius to obtain the intrinsic volume of the solute, n is the number of polar groups in the solute molecule and σ is the decreasing in volume produced by a mole of hydrogen bonds.

Applying that equation the authors were able to reproduce with a fair approximation the data for ϕ_V^O taking $\Delta=0.53$ or 0.57\AA and $\sigma=5,9 \text{ cm}^3 \text{ mol}^{-1}$.

As equation (5) accounts for the hydration of hydrophilic compounds it means that the most significant contribution to the volume comes from the polar groups.

In Table 2 we should note that different hexoses and pentoses have different ϕ_V^O . An explanation for this fact has been given in terms of differences in the behaviour of equatorial and axial OH groups. However, it is rather difficult to correlate the volume data with the number of hydroxyl groups in a certain position. According to their number of equatorial OH groups, the monosaccharides should follow the sequence

pentoses ribose < arabinose < xylose
hexoses manose < galactose < glucose .

As we can see in Table 2 it is not possible to correlate the volume data with these sequences.

Other effects will give a contribution to the volume. We believe that the sequence and extension of the polar and non-polar parts play an important role on hydration of this sort of solutes. (25)

Table 2 - van der Waals and apparent molal volumes at 25°C

	V_W^O ($\text{cm}^3 \text{ mol}^{-1}$)	ϕ_V^O ($\text{cm}^3 \text{ mol}^{-1}$)	Ref.
Methanol	21,7	38,25	9
Ethanol	31,9	55,12	9
1-Propanol	42,2	70,63	9
1-Butanol	52,4	86,48	9
Methylamine	24,2	41,68	9
Ethylamine	34,4	58,37	10
1-Propylamine	44,7	74,12	10
1-Butylamine	54,9	89,8	10
Formamide	25,5	38,532	10
Acetamide	35,7	55,824	11
Propanamide	45,9	71,540	11
Butanamide	56,1	87,1	12
1,2-Ethandiol	36,5	54,60	13
1,2-Propanediol	46,8	71,22	14
1,3-Propanediol	46,8	71,89	15
2,3-Butanediol	57,0	86,56	14
1,3-Butanediol	57,0	88,32	14
1,4-Butanediol	57,0	88,35	14
cis-1,2-cyclohexanediol	68,1	101,3	16
trans-1,2-cyclohexanediol	68,1	103,0	16
1,4-cyclohexanediol			
(cis-trans mixture)	68,1	105,3	17
Arabitol	81,0	103,0	18
Ribitol	81,0	103,2	18
Xylitol	81,0	102,4	18
Galactitol	95,8	114,3	14
Mannitol	95,8	119,33	14
Myo-inositol	86,5	121	19
Arabinose	70,1	93,2	18
Ribose	70,1	95,2	18
Xylose	70,1	95,4	18
Galactose	84,9	110,4	18
Glucose	84,9	112,04	20
Mannose	84,9	111,2	21
Cellobiose	157,4	213,6	21
Lactose	157,4	209,1	18
Maltose	157,4	208,8	21
Melibiose	157,4	204,0	21
Sucrose	157,4	211,6	18
Trehalose	157,4	206,9	21

Variation of volume with temperature

In systems where the magnitude of solvent-solute forces is similar to the thermal energy, important information about the nature and intensity of these forces can be obtained from the temperature coefficient of the volume. This coefficient can be determined by measuring the volume at different temperatures or by dilatometric measurements. (26)

Values of expansibility coefficients for several non-electrolytes can be found in literature, though to a less extension than data for the volume at a given temperature. Some of such data are shown in Table III.

Some conclusions have been withdrawn from thermal expansion data, and based on this property it has even been tried to classify the solutes as structure makers or structure breakers.

Neal and Goring (19) proposed such a classification by comparing the temperature coefficient of the apparent molar volume and that of the pure solute. Structure makers would be the solutes for which $d\phi_V^0/dT < dV_2^0/dT$ and structure breakers those for which $d\phi_V^0/dT > dV_2^0/dT$.

Butanol, cyclohexanol, tetrahydrofuran, tetrahydropyran belong to the first group while sucrose, glycerol, urea, formamide to the second one.

This relation admits that the intermolecular hydrogen bonds in the water under the influence of non-polar groups are weaker than those established between water and the polar groups. Another interpretation can be given assuming that hydrophobic hydration is not significant for the expansibility which is not surprising once its contribution to the volume is not meaningful.

Results obtained in our laboratory for sugars and polyalcohols show that the expansibility coefficient differs from compound to compound and varies appreciably with temperature. (25)

It has also been attributed a special meaning to the expansibility

coefficient with the temperature. Experimental results show that, for structure makers, $d^2\phi_V^0/dT^2 > 0$ and for structure breakers $d^2\phi_V^0/dT^2 < 0$ (see Table 3).

Research carried out in our group shows that it is not possible to characterize both types of hydration through the signal of the second derivative of the volume. Indeed, molecules so similar as monosaccharide conformers, can exhibit both signs for this derivative. $d^2\phi_V^0/dT^2$ is in fact an important quantity, not to differentiate the nature of the structure of the hydration, but rather to point out the strength of the forces involved. Actually $d^2\phi_V^0/dT^2 > 0$ means that the rate of loss of water is higher at lower temperatures, while $d^2\phi_V^0/dT^2 < 0$ means that the water is more firmly bound to the solute and the rate of loss increases with temperature.

The second derivative of the volume relative to temperature can be related with the heat capacity through thermodynamics as

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P \quad (6)$$

This equation has been used to classify the solutes by admitting that the rupture of intermolecular bonds of water by increasing pressure will occur only in hydrophobic hydration, to which then will correspond $d^2\phi_V^0/dT^2 > 0$. Hydrophilic hydration will give the opposite signal to this relation.

Variation of volume with pressure

The variation of volume with pressure is another property widely used in studies of hydration both in ionic and non-ionic solutes. As the increase in pressure gives rise to a reduction of the free volume of a liquid, naturally, the solvent molecules subject to weaker intermolecular forces are the most compressible. As an example, it is considered that the water in the primary hydration layer of an ion is incompressible,

once it is under a rather strong electric field.

The isothermic compressibility coefficient of a solution

$$\beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

can be determined by a direct process of P-V measurements. Such technique used in a pioneering work of Bridgeman et al (27) needs a high pressure special equipment and requires great care in order to obtain precise results (28) and it is not a good method for low pressures and dilute solutions.

An alternative method now being more used consists on the determination of compressibility from measurements of ultrasound velocities. (29) In this method the heat generated is not dissipated and therefore the compressibility coefficient is isentropic

$$\beta_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S \quad (7)$$

The isentropic compressibility coefficient is related to the velocity of ultrasound through Laplace equation

$$\beta_S = \frac{10^6}{u^2 d} \quad (8)$$

u is the velocity in cm s^{-1} and d the density of the solution.

If one admits that hydration water is incompressible, then we can calculate the hydration number from compressibility data. In fact, the volume of a solution with one mole of solute and n_1 moles of water is given by

$$V = \bar{V}_S^0 + h \bar{V}_{1,h}^0 + (n_1 - h) \bar{V}_1^0 \quad (9)$$

where \bar{V}_S^0 is the intrinsic volume of the solute, $\bar{V}_{1,h}^0$ the partial molar

volume of the hydration water and h is the hydration number.

Differentiating this equation in order to the pressure we obtain for dilute solutions the following expression for h

$$h = n_1 \left(1 - \frac{\beta_S}{\beta_{S,1}} \right) \quad (10)$$

Some results have been obtained for hydrophilic compounds by this method.

If one's objective is the study of the solute hydration it may be of greater interest to consider its partial molar compressibility or similarly to volume, the apparent molar compressibility $\phi_{K,S}$, given by

$$\phi_{K,S} = \frac{1000 (\beta_S - \beta_{S,1})}{m d_1} + \beta_{S,1} \phi_V \quad (11)$$

where the symbols have the previously indicated meanings.

As the solute-solvent interaction gives $\beta_S < \beta_{S,1}$, $\phi_{K,S}$ will decrease as the interaction forces will increase.

The isentropic compressibility can be related to a more used thermodynamic quantity, isothermic compressibility, by the expression

$$\phi_{K,T}^0 = \phi_{K,S}^0 + \frac{T \bar{V}_1^0 \alpha_1^0}{\bar{C}_{P1}^0} \left(2 \phi_E^0 - \frac{\bar{V}_1^0 \alpha_1^0 \bar{C}_{P2}^0}{\bar{C}_{P1}^0} \right) \quad (12)$$

α_1^0 is the expansibility coefficient of the water, \bar{C}_{P1}^0 and \bar{C}_{P2}^0 are the partial molal heat capacities of water and solute respectively and ϕ_E^0 is the apparent expansibility, that is, $\phi_E^0 = (\partial \phi_V^0 / \partial T)$.

Aqueous solutions of several non-electrolytes have been studied, namely amines (30) amides, urea and derivatives (20), mono- and polyhydric alcohols, (18,31) sugars (18), etc. The results of apparent molar compressibility at infinite dilution for some of those compounds are shown in Table 4.

Table 3 - Temperature coefficient of specific volumes of some compounds at 40°C (19)

Compound	$d\phi_2/dt \times 10^3$ (ml g ⁻¹ K ⁻¹)	$(dv_2/dt - d\phi_2/dt) \times 10^3$ (ml g ⁻¹ K ⁻¹)	$d^2\phi_2/dt^2 \times 10^4$ (ml g ⁻¹ K ⁻²)
1-Butanol	0,307	0,75	0,14
Cyclohexanol	0,489	0,27	0,18
Sucrose	0,734	-0,70	-0,29
Tetrahydrofuran	0,878	0,50	-0,06
Tetrahydropyran	0,914	0,38	0,00
Glycerol	0,941	-0,592	-0,09
i-Inositol	1,215	—	-0,23
Urea	1,711	-0,74	-0,24
Formamide	2,315	-1,651	-0,61

Table 4 - Isentropic partial molal compressibilities in aqueous solution at 25°C.

Compound	$\phi_K^O \times 10^4$ (cm ³ mol ⁻¹ bar ⁻¹)	Ref.
1-Propanol	5,8	31
1-Butanol	4,5	31
1,2-Propanediol	2,4	31
1,4-Butanediol	9,0	31
1,3-Butanediol	-0,1	31
2,3-Butanediol	6,9	31
Arabitol	-10,0	18
Ribitol	-9,6	18
Xylitol	-12,0	18
Galactitol	-14,6	18
Glucitol	-14,0	18
Mannitol	-14,9	18
Arabinose	-19,3	18
Ribose	-12,5	18
Xylose	-12,9	18
Galactose	-20,8	18
Glucose	-17,8	18
Mannose	-16,0	18
Lactose	-30,4	18
Maltose	-23,7	18
Sucrose	-17,8	18
Methylamine ⁱ⁾	4,5	30
Ethylamine ⁱ⁾	-2,5	30
1-Propylamine ⁱ⁾	-9,5	30
1-Butylamine ⁱ⁾	-16,0	30
1,4 dioxane	9,58	32
Dextrose	-17,50	32
D-Ribose	-12,46	32
Sucrose	-18,56	32

A rapid analysis of this table leads us to conclude that the apolar part of the solute molecule produces a decrease in the apparent molar compressibility. This behaviour becomes evident when we compare homologous compounds, monoamines, monoalcohols, etc. That is, series of compounds in which the polar group is the same, differing one from another by increasing the apolar part.

The contribution of polar groups, which we admit to be in the direction of a decrease in ϕ_K^O , does not come clearly from comparing the results of mono- with di-alcohols and of mono- with di-amines. Equally, it can be concluded that the effect of polar groups on ϕ_K^O is less than that of non-polar ones. However, if we admit that the polar and non-polar groups interfere with each other in the hydration, as mentioned before, then it is difficult to ascribe a certain contribution to a group. Hydrophilic molecules as monosaccharides and poly-alcohols have low values of $\phi_{K,S}^O$. To evaluate better the contribution of each group to ϕ_K^O we need to have data on compounds where the ratio between polar and non-polar groups be the widest possible. For example to evaluate the contribution of the polar part it is important to have data on di-, tri- and tetra-alcohols or on poly-amines.

Some authors have studied the compressibility at several temperatures and concentrations.^(20,30,33,35) The variation of compressibility with any of these parameters gives interesting results. The variation with temperature shows that compressibility increases with increasing temperature and the difference among compounds is reduced as temperature goes up. The variation with the concentration also gives information on the structure of the solute.

Lastly, we think we should refer that the compressibility does not show up detailed aspects on the hydration. For instance the differences between conformers in polyalcohols with five and six hydroxyl groups do not clearly show the differences in conformation. Also it is not easy to

see in monosaccharides any correlation between compressibility and the number of OH group in equatorial or axial positions.

Temperature of maximum density

As it is well known a solute that forms an ideal solution with water will give a lowering of temperature of maximum density. The temperature of maximum density of water is 3.98 C and then the lowering produced by the solute is

$$\Delta\theta_i = \theta - 3,98$$

where θ is the temperature of maximum density of the ideal solution thus formed.

If the solution is not an ideal one, the value of $\Delta\theta$ which it gives rise, can be considered as a sum of two terms, one corresponding to the ideal behaviour and the other to the effects produced in water by the introduction of the solute (structural effects).

$$\Delta\theta = \Delta\theta_i + \Delta\theta_{st}$$

If the solute is structure maker then $\Delta\theta_{st} > 0$ and if it is structure breaker $\Delta\theta_{st} < 0$.

Values of $\Delta\theta_{st}$ have been determined for some compounds as for linear and cyclic alcohols^(36, 37). Very few studies were done for hydrophilic molecules.

Conclusion

From what we have said we may conclude that there are still many points to clarify concerning the interaction of hydrophilic solutes with water.

Volumetric properties that have been widely used in such studies have given some relevant data and they seem to show up details of solute-solvent interactions like those from the conformation of the solute molecule. However their quantitative interpretation has been difficult to achieve.

The existence of polar and non-polar groups in the solute molecule makes this study more difficult, being necessary to have data on different types of compounds and for different properties in order to build up a structural model of these solutions.

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