

Water Sorption, Binding and Solubility of Polyols

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The sorption of water by polyhydroxyalkanes and polyalkylene glycols has been studied at 35°C and 75% relative humidity. The solubilities in water of these compounds were taken from the literature or measured by us, and found to be predictable from Yalkowski's expression and to correlate with the water sorption ability, with some notable exceptions, rationalized with reference to the configurations of the compounds in question. In very concentrated aqueous solutions all the water is bound to the polyols; in dilute solutions two or four molecules of water are bound per oxygen atom of the polyhydroxyalkanes and polyethylene glycols, respectively.

A limited amount of information is available on the water sorption abilities of certain polyols: linear polyhydroxyalkanes and polyalkylene glycols, cf. Scheme 1. For a few¹ this information is available as a function of the temperature and the relative humidity. However, there is little comparative information on this property at a given temperature and relative humidity, that would allow a judgement of their relative merits as humectants and moisturizers.

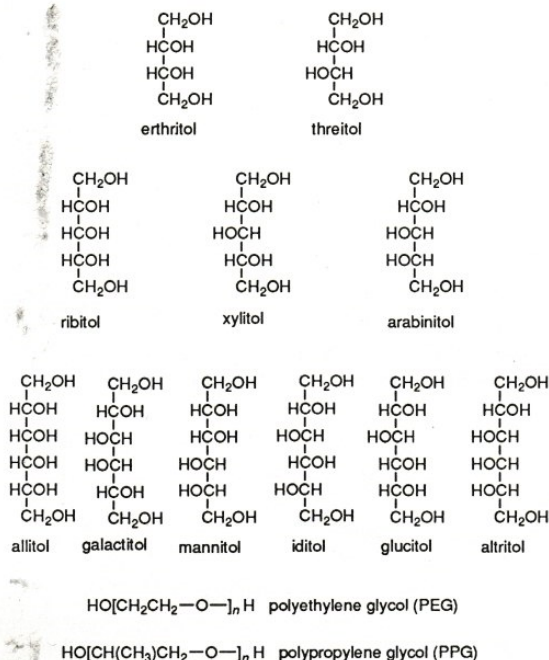
When a solid polyol absorbs water it generally deliquesces and becomes a concentrated aqueous solution. A liquid polyol forms such a solution in the first place. The smallest polyols [ethane-1,2-diol, glycerol and polyethylene glycols (PEGs) up to and including molar weight 600], are miscible with water in all proportions, i.e. they have an infinite solubility in water. The others may have a large but finite solubility. The state of the water in the concentrated solutions at

equilibrium with the solid or with a humid atmosphere, i.e. how much of it is bound to the polyol and how much is free, has not been determined yet. This should have a bearing on the water sorption properties of the compounds. Finally, it is noted that configurational isomers of certain polyols may have widely different water sorption properties. This point should be discussed in relation to the detailed structures and conformations of these compounds.

In the present study, the water uptake (weight gain) at equilibrium of a wide variety of polyhydroxyalkanes and polyalkylene glycols was determined by the isopiestic method at $35 \pm 2^\circ\text{C}$ and a relative humidity of 75% (actually $75.1 \pm 0.1\%$). This relative humidity was obtained by using as the isopiestic reference a saturated solution of sodium chloride.² The relative amount of bound water was determined by the method of Bonner and Woolsey³ from the differential light absorption at 958 nm of concentrated aqueous solutions of the polyols. This absorption corresponds to a vibrational combination band of water, $2\nu_1 + \nu_3$, that is said to be sensitive solely to the free, monomeric form of water. The solubilities of some of the polyols not given in the literature were also measured (at 25°C).

Experimental

The isopiestic method consists of bringing ca. 1 g of the studied materials to thermal and vapour pressure equilibrium, placed in small weighing vessels, with a large reservoir of saturated aqueous sodium chloride in a confined enclosure. This enclosure, a large desiccator, is partly immersed in a constant-temperature water bath, its upper part being well thermally isolated, and the temperature in its interior ($35 \pm 2^\circ\text{C}$) being measured with a thermometer in the vapour space. As the materials take up water from the vapour space the saturated salt solution loses water by evaporation and sodium chloride precipitates. This process is reciprocal, however, so that excess water from the materials can transfer through the vapour space, condense in the sodium chloride solution, and cause more salt to dissolve. At equilibrium these two processes balance. Occasional gentle shaking of the vessel helps the attainment of equilibrium, overcoming the viscosity of the resulting concentrated solutions. All the materials studied have such low vapour pressures,¹ compared with water, that they themselves do not evaporate during the measurements that take several days. Pumping is applied to the vapour space at the beginning of each run, in order to shorten the free pathlength of the water



Scheme 1

Table 1 Water gain (wt.%), number of moles of water sorbed per mole of solute, n_{ws} , and per mole of oxygen atoms in the solute, n_{ws}/n_o , for polyols at 35 °C and 75% relative humidity

no.	compound	water gain (wt.%)	n_{ws}	n_{ws}/n_o
polyhydroxyalkanes:				
1	ethane-1,2-diol	41.9	1.44	0.72
2	glycerol	51.5	2.63	0.89
3	threitol	64.1	4.34	1.09
4	erythritol	0.5	0.03	0.0
5	xylitol	35.9	3.03	0.61
6	ribitol	9.0	0.76	0.15
7	arabinitol	38.0	3.21	0.64
8	galactitol	0.0	0.00	0
9	mannitol	ca. 0	ca. 0	0
10	glucitol	21.4	2.16	0.36
polyethylene glycols:				
11	diethylene glycol	43	2.53	0.87
12	PEG 200	36.7	3.96	0.80
13	PEG 300	33	5.50	0.73
14	PEG 400	27.5	6.11	0.65
15	PEG 600	22	7.33	0.54
16	PEG 1000	23.5	3.1	0.45
17	PEG 1450	20	6.1	0.47
18	PEG 2000	13.2	4.7	0.32
19	PEG 3000	5.8	9.7	0.14
20	PEG 4000	0	0	0
polypropylene glycols:				
21	dipropylene glycol	12	0.89	0.33
22	PPG 425	7.7	1.81	0.19
23	PPG 725	3.2	1.29	0.11
24	PPG 1000	2.9	1.61	0.09

molecules in the vapour and expedite the initial transfer of water from the salt solution. At intervals, the enclosure is opened, the small vessels are closed and weighed, then opened, returned to the enclosure, and the process is continued until constant weight (within 2%) is attained. All experiments are carried out in duplicate, with agreement within 2% (sample + water) between duplicates.

Differential light absorption measurements were made at 958 nm with a Cary 14 instrument at room temperature ($23 \pm 2^\circ\text{C}$). In spite of the older technology involved with this spectrophotometer, there is no practical alternative for work at this wavelength. Two matched 10.00 cm pathlength cells were employed, one filled with water (in the sample beam) and the other filled with the solution (in the reference beam, in order to obtain positive signals). The densities of the solutions were determined picnometrically to 0.001 g cm^{-3} . The working equations for obtaining the number n_B of water

Table 2 Compositions (wt.%) of polyol solutions, the total number of moles of water per mole of oxygen atoms of solute, n_{w}/n_o , and the number of moles of bound water per mole of oxygen atoms of solute, n_B/n_o

no.	compound	wt.%	n_{w}/n_o	n_B/n_o
1	ethane-1,2-diol	29.9	8.08	1.94
		37.6	5.74	1.95
		46.6	3.97	1.65
		56.3	2.69	1.30
		64.4	1.90	1.02
2	glycerol	42.9	2.27	1.51
		51.1	1.63	1.32
		61.7	1.06	0.93
		70.0	0.73	0.73
		79.2	0.45	0.37
4	erythritol	9.3	16.59	1.68
		18.9	7.30	1.19
		27.6	4.45	1.66
		36.3	2.98	1.46
		44.0	2.15	1.28
5	xylitol	18.2	7.62	1.35
		27.5	4.46	1.11
		35.6	3.07	1.31
		44.0	2.15	1.28
		50.6	1.65	0.99
10	glucitol	16.0	8.84	0.92
		28.4	4.24	1.20
		39.4	2.59	1.18
		21.5	7.88	2.86
		25.9	6.17	2.67
12	PEG 200	39.6	3.29	2.28
		45.0	2.64	2.04
		57.7	1.62	1.58
		28.1	5.99	3.37
		36.9	4.00	2.80
14	PEG 400	44.4	2.94	2.45
		55.1	1.95	1.90
		63.8	1.33	1.49
		8.0	27.15	1.98
		16.7	11.81	2.50
16	PEG 1000	23.5	7.69	2.92
		32.4	4.93	2.54
		37.6	3.92	2.39
		8.3	26.63	2.93
		16.1	12.58	3.42
18	PEG 2000	23.1	8.04	3.15
		32.2	5.09	2.82
		38.0	3.94	2.57
		8.8	24.98	4.20
		16.5	12.21	3.86
19	PEG 3000	25.6	7.01	3.49
		32.3	5.06	3.18
		40.3	3.58	2.71

molecules bound per molecule of solute are:^{3,4}

$$n_B = 55.51y/m \quad (1)$$

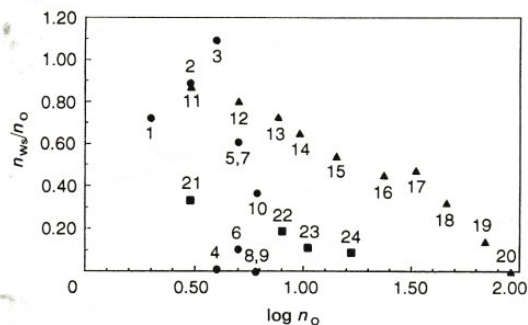
where 55.51 is the number of moles of water and m the number of moles of solute per kg of water. The fraction y of water bound is assumed³ to equal the fraction of monomeric water, given in turn by:

$$y = [0.75(1 - f) - A_{\text{diff}}]/0.55 \quad (2)$$

where A_{diff} is the differential absorbance (for the 10 cm cell) and f is the volume fraction of water in the solution. The numerical constants are the absorbances of the hydrogen-bonded and monomeric water.³ The fraction f is given by:

$$f = d_{\text{solution}} / \{d_{\text{water}}[1 + m(M_{\text{solute}}/\text{kg mol}^{-1})]\} \quad (3)$$

where d denotes density and the second factor in the denominator is the weight of the solution in kg, M_{solute} being the molar mass of the solute. From errors in the reading of A_{diff} from the spectra of 958 nm, not necessarily the peak of the

**Fig. 1** Number of water molecules sorbed per oxygen atom of the polyol, n_{ws}/n_o , vs. $\log n_o$. ●, Polyhydroxyalkanes; ▲, polyethylene glycols; ■, polypropylene glycols. The numbers correspond to the compounds in Table 1.

absorption band, the precision of the resulting n_B values is $\pm(10-15)\%$.

The aqueous solubilities of D,L-threitol, xylitol, ribitol and D,L-arabinitol and of PEG-2000 and PEG-3000 were measured at $25.0 \pm 0.2^\circ\text{C}$ by contacting excess solute with the aqueous solution until constant composition of the latter was achieved (2-3 days). The composition was determined by weight after evaporation of all the water in vacuum at 60°C to produce a free-flowing solid. The densities of the saturated solutions, for conversion to the molar scale, were also measured.

Results

The water gain of the polyols (wt.%) and also converted to moles water sorbed per mole polyol, n_{W_s} , at equilibrium at 35°C and 75% relative humidity is shown in Table 1. In Fig. 1 n_{W_s} has been divided by n_O , the number of oxygen atoms per molecule of the polyol, and is plotted against $\log n_O$ (the values of n_O range from 2 in ethane-1,2-diol to 94 in PEG 4000). The numbers identifying the experimental points refer to Table 1. The very low water sorption by erythritol, ribitol, mannitol and galactitol should be noted, as also the much lower sorption of water by the polypropylene glycols than by the polyethylene glycols.

The compositions (wt.%) of the concentrated solutions of the polyols in which the relative amount of bound water has been measured are shown in Table 2. These quantities are converted to the total number of moles of water per mole of solute, n_{W_t} , divided by n_O and are also shown in Table 2, together with the ratios of the number, n_B , of bound water molecules per molecule of polyol to n_O . These results are plotted in Fig. 2. The densities of the concentrated polyethyl-

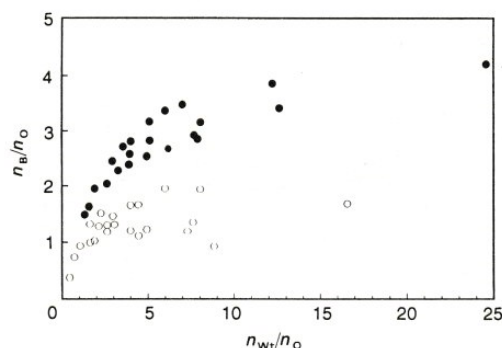


Fig. 2 Number of water molecules bound per oxygen atom of the polyol, n_B/n_O , vs. the total number of water molecules present in the solution per oxygen atom of the polyol, n_{W_t}/n_O . ●, Polyethylene glycols; ○, alditols.

ene glycol solutions conform to the expression:

$$d = 0.982 + 0.0025 \text{ wt.}\% + 8.3 \times 10^{-6} \text{ wt.}\%^2 \quad (4)$$

Table 3 summarizes the published solubilities of the compounds studied here as well as the present determinations, as g solute per 100 g water, s_{W_t} , and as $\log s$ (the molar solubility).

Discussion

Table 1 shows several interesting features, besides the general trend of decreasing values of the water gain as the number of ethylene oxide or propylene oxide monomeric units in the polyethylene (PEG) and polypropylene (PPG) glycols increases. Foremost among these is the strong dependence of

Table 3 Solubility of the polyols (with specified melting points, t_m) in water at 25°C unless otherwise noted: s_{W_t} , converted to s_{expt} by means of estimated densities, and values of s_{calc} , from eqn. (6)

no.	compound	$t_m/^\circ\text{C}$	$s_{W_t}/\text{g (100 g H}_2\text{O)}^{-1}$	$\log(s_{\text{expt}}/\text{mol dm}^{-3})$	$\log(s_{\text{calc}}/\text{mol dm}^{-3})$
polyhydroxyalkanes:					
1	ethane-1,2-diol	-13^a	∞		
2	glycerol	20^a	∞		
3	D,L-threitol	90^b	880^c	0.97	0.97
4	erythritol	120^d	63.7^d	0.57	0.67
5	xylitol	94.5^e	179^e	0.74	0.77
6	ribitol	102^e	151^e	0.67	0.69
7	D,L-arabinitol	103^e	211^e	0.71	0.68
	D-iditol	75^e	449^a	0.80	0.79
	D,L-altritol	96^e			0.59
8	galactitol	198^e	3.2^e	-0.74	-0.42
9	D,L-mannitol	166^e	22^e	0.01	-0.11
10	D-glucitol	112^f	75^f	0.45	0.43
10	D,L-glucitol	136^e			0.20
	allitol	155^e			0.00
polyethylene glycols:					
11	diethylene glycol	-8^a	∞^a		
	triethylene glycol	-7.2^a	∞^a		
12-15	PEG ≤ 600	$\leq 25^a$	∞^a		
16	PEG 1000	ca. 41^a	ca. 230^a	-0.23	-0.24
17	PEG 1450	ca. 46^a	ca. 230^a	-0.39	-0.41
18	PEG 2000		158^c	-0.51	-0.54
19	PEG 3000		148^c	-0.67	-0.72
20	PEG 4000	ca. 56^a	ca. 160^a	-0.87	-0.84
polypropylene glycols:					
21	propane-1,2-diol		∞^a		
	dipropylene glycol		∞^a		
22	PEG 425	-60^a	∞^a		
23	PPG 725		18.1^a	-0.67	
24	PPG 1000	-50^a	1.5^a	-1.83	

^a Ref. 1. ^b Ref. 16. ^c This work. ^d Ref. 14. ^e Ref. 17. ^f Ref. 15.

the water sorption of the polyhydroxylalkanes on their steric configuration. Among the tetrithols, the chiral but racemic D,L-threitol [(R*), (S*)-1,2,3,4-butanetetrol] sorbs a large amount of water whereas the *meso*-isomer erythritol [(R*), (R*)-1,2,3,4-butanetetrol] hardly sorbs water at all. Considerable differences are also seen among the pentithols: xylitol being much more hygroscopic than ribitol, and again among the hexithols: iditol (not readily available commercially) is said⁵ to be very deliquescent, glucitol is only moderately hygroscopic,⁶ and mannitol and galactitol are hardly hygroscopic at all.

It is intuitively conceivable that the water sorption properties of the polyols may be related to their aqueous solubilities and their abilities to bind the water in concentrated solutions. This hypothesis is examined in the following. As already mentioned, the smallest compounds of the homologous series have infinite solubilities. In the cases of some of the alditols there are polymorphic varieties (*e.g.* xylitol has a metastable low-melting-point form), and even pure enantiomers may have solubilities different from their racemic mixtures (*e.g.* glucitol). In some cases the solubilities are so large and the solutions so viscous that the resulting values are rather uncertain.

For those cases where the solubility is finite, it is of interest to examine the applicability of the correlation reported by Yalkowsky *et al.*⁷ for a great variety of organic solutes. They have demonstrated a correlation of the logarithm of the molar (mol dm^{-3}) aqueous solubility, $\log s$, with the melting point ($^{\circ}\text{C}$), t_m , of solid solutes (for liquids t_m is set equal to 25°C), the intrinsic molecular volume, V_i , and the electron-pair donation (hydrogen-bond acceptance) ability of the solute, β . The relevant expression is:

$$\log s = 0.86 - 0.062V_i - 0.0099(t_m - 25) + 4.9\beta \quad (5)$$

This expression, excluding consideration of strong hydrogen-bond-donor solutes, was based on work of Kamlet *et al.*⁸ The latter workers, however, did consider such solutes too, and added a term in their hydrogen-bond-donation ability, α , so that the last term in the modified eqn. (5) reads⁸ as in eqn. (6) instead of 4.9β :

$$\log s = 0.86 - 0.062V_i - 0.0099(t_m - 25) + (3.84\beta + 1.59\alpha) \quad (6)$$

The molar solubility s must be calculated from the published values of s_w , $[\text{g (100 g water)}^{-1}]$ by means of the densities of the saturated solutions. These densities are not known, and it is assumed that they are approximately the same as the tabulated⁹ values of sucrose solutions of the same percentage composition. Leahy's intrinsic molecular volumes V_i ¹⁰ are calculated from the linear correlation function:

$$V_i = 1.8 + 0.674V_x \text{ cm}^3 \text{ mol}^{-1} \quad (7)$$

and found¹¹ to apply for V_x values calculated from the atomic constitution and the number of bonds according to Abraham and McGowan:¹²

$$V_x = 16.35n_c + 12.43n_o + 8.71n_H - 6.65n_{\text{bonds}} \text{ cm}^3 \text{ mol}^{-1} \quad (8)$$

Kamlet and Taft's α and β values are not known for the polyols as solutes. They are associated in the liquid form (for which some α and β values are known), but the nature of the hydrogen bonding taking place there is not different from that in the saturated aqueous solutions. It is assumed, therefore, that the required β values can be estimated from the values for liquid water (0.47), ethane-1,2-diol (0.52), and glycerol (0.51)¹³ as 0.50 ± 0.02 , independent of the number of OH groups of the alditol. The values of α for ethane-1,2-diol (0.91) and glycerol (1.23)¹³ point to a dependence of α on the number of OH groups, n_{OH} . The following is based on the assumption that $\alpha = (0.43 \pm 0.02)n_{\text{OH}}$. The contribution of

the modified last term in eqn. (6) is then $(1.92 \pm 0.07) + (0.68 \pm 0.03)n_{\text{OH}}$.

The uncertainties in $\log s_{\text{expt}}$, due to experimental difficulties and the use of aqueous sucrose to estimate the densities, are expected to be ± 0.05 . Values of $\log s_{\text{calc}}$ calculated from the modified eqn. (6) are shown in Table 3. Uncertainties in the melting points of $\pm 1^{\circ}\text{C}$ and in the intrinsic volume term of $\pm 1\%$ [due to the correlation (7)¹¹] have only a minor effect, and the main uncertainty of $\log s_{\text{calc}}$ resides in the combined α and β term. Agreement of the calculated with the experimental values¹⁴⁻¹⁷ within the uncertainties is seen to have been achieved, except for the case of galactitol, which is two times less soluble than expected.

The quantitative considerations on which eqn. (5) or (6) is based are not applicable to the polyalkylene glycols. Although values of $\log s$ can be obtained from the wt.% solubility, the density and the average molar weight, these materials are mixtures, hence composition-weighted values for some terms in the equations are required that cannot be readily calculated. Even if the average composition is taken to represent such a material, the intrinsic molar volumes estimated *via* eqn. (7) and (8) are so large (*e.g.* ca. $530 \text{ cm}^3 \text{ mol}^{-1}$ for PEG 1000), that the term in eqn. (6) pertaining to it and decreasing the solubility becomes incommensurate with $\log s$. This large term should be compensated to a large degree by the last term in eqn. (6), since the ethereal oxygen atoms in the polyalkylene glycols ought to act individually to increase the solubility, but no quantitative estimate of this can be proposed. In a crude manner, the solubilities of the PEGs are given by $\log s = 2.76 - \log M$, where M is the nominal molar mass. The solubilities of the PPGs are considerably lower, but too few values have been reported to make a generalization possible.

Whether or not a correlation exists between the abilities of the polyols to sorb water and their aqueous solubilities is seen in Fig. 3, where n_w/n_o is plotted against the quantity $-(RT \ln s)/\text{kJ mol}^{-1}$. In those cases where there are no actual solubility data, s was calculated as described above (including values for the water-miscible ethane-1,2-diol and glycerol as well as the smaller PEGs). On the whole, the higher the solubility [the more negative $-(RT \ln s)]$, the higher the ability to sorb water. The two hexithols, mannitol and galactitol, do not have very appreciable solubilities in water nor do they sorb water, and their behaviour more or less conforms to expectation. Very notable exceptions are the non-chiral erythritol and ribitol: their solubilities are quite high, but they hardly sorb water at all. In fact, erythritol can be used for cake icing, due to its sweetness but negligible hygroscopicity.¹⁸ In contrast, its isomer, threitol, sorbs water quite well and forms a peak in the curve in Fig. 3. The reason

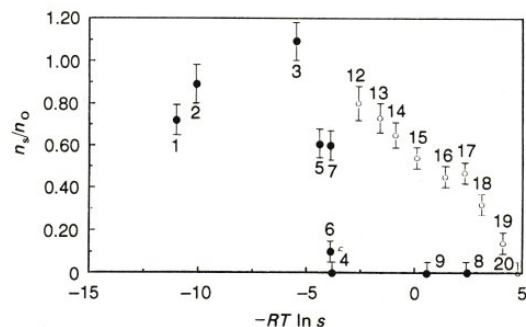


Fig. 3 n_w/n_o , vs. $-RT \ln s$ of the polyol. ●, Polyhydroxyalkanes; ○, polyethylene glycols. The numbers correspond to the compounds in Table 3.

for this difference between the isomers ought to be sought in the different configurations¹⁹ of the adjacent hydroxy groups: *gauche-trans-gauche* in crystalline erythritol²⁰ and *trans-gauche-trans* in crystalline threitol.²¹ The latter may in solution revert to *gauche-parallel-gauche*, forming a pocket of four OH groups pointing in the same general direction which is able to bind water more readily by a cooperative effect. This configuration is not available to erythritol in solution by any rotation around the C—C bonds. Similar, but less striking, differences are observed for the pentitols (xylitol *vs.* ribitol) and hexols (glucitol *vs.* galactitol), if they are optically active (sorbing much water) or inactive (sorbing only small amounts of water).

The binding of the water to polyethylene glycols in dilute solutions is seen in Fig. 2 to approach four molecules of water per atom of oxygen in the solute. When the excess of water present in the more concentrated solutions diminishes, this ratio decreases, and in very concentrated solutions there remains no free water at all. The polyhydroxyalkanes appear to bind fewer water molecules than the PEGs in the less concentrated solutions, their number appearing to approach two at high dilutions. Mannitol, at 2 wt.% and $n_w/n_o = 86$ was found⁴ to bind $n_b/n_o = 1.80$ molecules of water per oxygen atom of the solute. Again, in highly concentrated solutions most of the water is bound. It is also noteworthy that erythritol binds relatively less of the water available to it than the other alditols tested. The reason should be the same as that noted above.

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