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Enthalpies of dilution of aqueous solutions of *n*-butanol, butanediols, 1,2,4-butanetriol, and 1,2,3,4-butanetetrol at 298.15 K

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Abstract

Enthalpies of dilution of aqueous solutions of 1-butanol, butanediols, 1,2,4-butanetriol and 1,2,3,4-butanetetrol (erythritol), were measured at 298.15 K, using a LKB flow microcalorimeter. Experimental data were treated according to the McMillan–Mayer theory, to obtain the enthalpic interaction coefficients. The pair interaction coefficient h_{xx} shows a clear dependence on number and position of OH groups. Results are discussed in terms of molecular interactions.
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Keywords: Enthalpies of dilution; Molecular interactions; Enthalpic interaction coefficients; Alcohols; Polyols

1. Introduction

The thermodynamic properties of aqueous solutions of alcohols and polyols are of special importance in the elucidation of the nature of interactions between nonpolar and polar groups and water and because of their connection with biological systems. It is well known that small alcohols act as protein denaturating agents while polyols and sugars are known to act as protein stabilizers and cryoprotectants for plant and animal tissues. Some studies suggest that the cryoprotective nature of polyols depends on the number and position of hydroxyl groups. However, the behavior of this type of solutes in water is not well understood due to the complexity of solute–water and solute–solute interactions that take place in aqueous solutions [1–4].

In a mixture, molecular interactions occur between both like and unlike molecules. A full description of a binary solution requires information about solvent–solvent, solvent–solute, and solute–solute interactions. The McMillan–Mayer solution theory [5] allows the formal separation of effects, which arise from molecular pair, triplet and higher order interactions. The magnitude and sign of solute–solute interactions are related to the changes in thermodynamic properties when two solvated solute molecules interact with each other. They can be analyzed in terms of the values of interaction coefficients obtained from experimental quantities in different ways. Many authors have assumed that the intermolecular energy is equal to the sum of two-body and three-body interactions for binary mixtures, but it should be noted that the contribution of three-body interactions is small compared to that of two-body interactions. Higher order interactions are generally negligible [6–9].

In this work we present a systematic study of the enthalpy of dilution and the virial enthalpic coefficients for aqueous solutions of 1-butanol, butanediols, 1,2,4-butanetriol and 1,2,3,4-butanetetrol (erythritol) in water. The alcohols were chosen to examine the effect of the increase in the number of OH groups as well as their

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position effect in the enthalpic coefficients of the alcohols in water.

The McMillan–Mayer theory [5] was employed to relate the experimental values of the dilution enthalpy with solute molality and to obtain the pairwise interaction coefficients of 1-butanol, butanediols, 1,2,4-butanetriol and 1,2,3,4-butanetetrol in water.

2. Experimental

The materials used in this work were the following: 1-butanol (J.T. Barker), 1,2-butanediol (Aldrich), 1,3-butanediol (Sigma), 2,3-butanediol (Fluka), 1,4-butanediol (Aldrich), 1,2,4-butanetriol (Fluka) and 1,2,3,4-butanetetrol (erythritol) (Sigma). The alcohols and polyols were of the highest commercially available purity and were degassed and maintained in desiccators before use. Water content was determined in all cases by the Karl Fischer method. Water was doubly distilled, treated according to literature and degassed before use. All solutions were prepared by weight using a Mettler balance AT-261 dual range with sensitivity of 10^{-5} g in the lower range. Final concentrations were corrected according to water content analysis.

Measurements of heats of dilution were carried out at $298.15 + 0.01$ K. The applied flow-calorimeter (type 10700–1, LKB, Bromma/Sweden) was used in the mixing mode. It was pre-thermostated by a cryothermostat (Colora Kryo-Thermostat WK5) set to 5 K below the working temperature of the instrument. The inflowing solution and water were brought to the correct working temperature in two thermostating coils before they met at the mixing point of a 0.56 ml heat exchanger spiral. Two peristaltic pumps were used: Pharmacia LKB P-2 and Biotech LP 80-A. The flow rates were determined by weighing the masses of liquids passing through the pumps in a given time. The Biotech pump was set to a fixed water flow of 6.63×10^{-3} g s^{-1}. The Pharmacia pump was used in variable mode with pumping speeds between 3.28×10^{-3} and 3.33×10^{-2} g s^{-1}. It was adjusted in such a way that all dilution heat had been dissipated to the heat sink before the mixed solutions left the spiral. The sensitivity of the microcalorimeter amounted to 100 μV mW^{-1}. The calorimetric signal was registered by a Hewlett Packard multimeter 34401A, which measures up to 1000 V with 6.5 digits resolution and accuracy in the order of 0.002%.

3. Results and discussion

The experimental results for the enthalpies of dilution of 1-butanol, 1,2-butanediol, 1,3-butanediol, 2,3-butanediol, 1,4-butanediol, 1,2,4-butanetriol and 1,2,3,4-butanetetrol (erythritol) in water are reported in Table 1. In all cases the relative standard deviation is less than 1 J mol^{-1}.

Table 1
Enthalpies of dilution of alcohols in water at 298.15 K

m_i[a]	m_f[a]	ΔH_{dil}[b]	m_i[a]	m_f[a]	ΔH_{dil}[b]
1-Butanol					
1.0923	0.5208	−848.4	0.5661	0.2788	−337.2
0.9408	0.4492	−691.2	0.5649	0.2710	−324.2
0.8837	0.4225	−615.4	0.5130	0.2462	−300.1
0.8401	0.4016	−572.8	0.5066	0.2431	−287.0
0.7526	0.3603	−508.1	0.5006	0.2403	−402.5
0.7521	0.3601	−533.7	0.3805	0.1829	−213.1
0.6796	0.3254	−426.4	0.3033	0.1460	−171.3
0.6772	0.3243	−440.4	0.1861	0.0921	−107.3
1,2-Butanediol					
5.2030	2.0633	−2705.8	1.7288	0.7868	−865.0
4.5069	1.8345	−2379.6	1.4991	0.6890	−719.4
3.9404	1.6392	−2141.8	0.9705	0.4564	−446.2
3.3040	1.4093	−1772.0	0.7251	0.3447	−328.5
2.6418	1.1574	−1393.6	0.5129	0.2461	−213.1
2.3694	1.0497	−1221.7	0.4728	0.2273	−201.2
			0.3181	0.1540	−129.4
1,3-Butanediol					
5.1371	1.9691	−2023.3	1.4820	0.6596	−561.1
4.3911	1.7322	−1749.5	0.9636	0.4390	−348.7
3.3028	1.3608	−1311.3	0.7361	0.3388	−257.1
2.7568	1.1617	−1109.4	0.5851	0.2712	−193.5
2.4317	1.0389	−953.9	0.4979	0.2317	−150.5
1.7357	0.7640	−668.3	0.4506	0.2101	−142.8
1,4-Butanediol					
6.3088	2.3151	−1820.8	2.8693	1.2035	−1033.3
5.9390	2.2092	−1795.3	2.7561	1.1615	−993.8
5.2385	2.0000	−1639.2	2.6236	1.1118	−943.9
5.0193	1.9326	−1531.9	2.4368	1.0408	−881.1
4.9667	1.9162	−1521.6	2.4015	1.0273	−874.3
4.6627	1.8800	−1558.1	1.7727	0.7791	−655.0
4.6260	1.8083	−1445.3	1.5963	0.7070	−596.1
4.3605	1.7222	−1415.6	1.4756	0.6570	−511.8
3.9837	1.5970	−1337.1	1.1837	0.5339	−405.9
3.64830	1.4822	−1258.7	1.0332	0.4692	−353.3
3.4218	1.4030	−1199.4	0.8801	0.4024	−269.2
3.0943	1.2858	−1100.5	0.6734	0.3108	−234.2
2,3-Butanediol					
4.2572	1.7430	−1905.0	0.8388	0.3954	−302.2
3.7334	1.5600	−1747.8	0.7651	0.3619	−268.5
3.3033	1.4040	−1449.7	0.7085	0.3359	−251.2
3.2549	1.3861	−1429.4	0.6375	0.3032	−233.0
2.0031	0.8980	−841.6	0.5972	0.2846	−208.6
1.5591	0.7123	−644.3	0.5103	0.2441	−158.5
1.2251	0.5678	−485.2	0.2858	0.1381	−97.1

m_i[a]	m_f[a]	ΔH_{dil}[b]
1,2,4-Butanetriol		
3.7991	1.4939	−989.4
3.1969	1.2928	−885.4
2.5892	1.0780	−756.5
1.9688	0.8452	−593.9
1.4006	0.6188	−424.5
0.8247	0.3755	−245.2
0.2751	0.1290	−52.2
1,2,3,4-Butanetetrol		
0.7919	0.3754	−15.6
0.6904	0.3292	−13.7
0.5988	0.2871	−12.9
0.4977	0.2401	−10.5
0.3995	0.1938	−7.9

[a] Units: mol kg^{-1}.
[b] Units: J mol^{-1}.

Table 2
Virial enthalpic coefficients of alcohols and polyols in water, at 298.15 K

Solute	h_{xx}[a]	h_{xxx}[b]	h_{xxxx}[c]	Δm[d]	Reference
1-Butanol	926	334		1.0923–0.0921	This work
	1003 ± 15	646 ± 56			[9]
1,2-Butanediol	777	73	−10	5.2030–0.1540	This work
	923	60		1.5310–0.0934	[16]
1,3-Butanediol	621	33	−5	5.1371–0.2101	This work
	1353	14		0.1547–0.01828	[10]
	750	14		0.8971–0.1263	[16]
1,4-Butanediol	705	−19	−1	6.3088–0.3108	This work
	2078	−8		0.1568–0.07044	[10]
	787	−8		1.202–0.2094	[16]
	657 ± 12			0.04–0.02	[17]
2,3-Butanediol	619	6951	−9	4.2572–0.1381	This work
	2766	51		0.09252–0.00998	[10]
	837 ± 10	51 ± 9		2.4679–0.0549	[18]
1,2,4-Butanetriol	524	20	−9	3.7991–0.1290	This work
1,2,3,4-Butanetrol	44	−5		0.7919–0.1938	This work
	398	−53			[16,19]
	359	−11			[16,20]

[a] Units: $J\,kg\,mol^{-2}$.
[b] Units: $J\,kg^2\,mol^{-3}$.
[c] Units: $J\,kg^3\,mol^{-4}$.
[d] Units: $mol\,kg^{-1}$.

According to the treatment proposed in the McMillan–Mayer theory of solutions, the dilution enthalpy for a binary mixture can be expressed as a virial expansion of solute molalities, in such a way that the coefficients characterizing the interactions between solute molecules can be obtained [10–12] from the following equation, fitting the experimental data by least squares:

$$\Delta H_{dil} = h_{xx}(m_f - m_i) + h_{xxx}(m_f^2 - m_i^2) + h_{xxx}(m_f^3 - m_i^3)$$

The homotactic coefficients h_{xx}, h_{xxx} and of higher order describe solute–solute interactions between solvated molecules, while m_i, and m_f represent the initial and final solute molalities, respectively. The interactions between polar non-electrolyte molecules include: (1) dipole–dipole interaction between polar groups, (2) hydrophobic–hydrophobic interaction between alkyl groups, (3) polar–apolar interactions between the solvated polar groups and solvated apolar alkyl groups. Besides, these interactions occur between solvated molecules, so that they are affected differently in the concentration range used [13,14].

The enthalpic coefficients obtained in this work and the concentration ranges are presented in Table 2 and compared with those reported in literature. In this work, the hydrocarbon chain remains constant and the number and position of OH groups varies. As the concentration range used in each case is wide except for erythritol due to solubility limitations, the adjustment by least squares was done to obtain the best fitting of the experimental data obtaining two or three coefficients. However, due to the large uncertainty in the higher order coefficients h_{xxx} and h_{xxxx} the analysis is restricted to the first pairwise coefficient h_{xx}.

In the pairwise association of alcohols and polyols, interactions involving the side-chains are significant and affected by the number and position of the OH groups. Table 2 shows that the pair enthalpic interaction coefficient, h_{xx}, between two alcohol molecules, is positive for all the systems studied. The highest h_{xx} value is for 1-butanol in agreement with results presented by other authors who have studied this system. The values become smaller as the number of OH groups increases [13–15]. The results obtained in this work for diols are consistent with those reported by most authors. The small differences can be attributed to the differences in the concentration range used and the resulting differences in least squares fitting of experimental data, with exception of the h_{xx} values reported by Fujisawa et al. [10] which are quite high. No results have been found in literature for 1,2,3-butanetriol and the value reported for 1,2,3,4-butanetetrol is much higher than our result [16].

The h_{xx} values decrease as the number of OH groups increases, in the following order: 1-butanol > 1,2-butanediol > 1,4-butanediol > 1,3-butanediol > 2,3-butanediol > 1,2,4-butanetriol > 1,2,3,4-butanetetrol.

The positive value of the enthalpic coefficient can be interpreted as the result of different contributions. In first place the polar–polar interaction between OH groups strongly hydrated with water that can participate in hydrogen-bonding interactions and have a negative contribution to h_{xx}. The endothermic effect due to partial dehydration of the solvation layers, characterized by a positive contribution to h_{xx}.

Finally, hydrophobic interactions involving apolar chains are also characterized by a positive contribution to h_{xx}.

The observed trend shows that the pairwise enthalpic coefficient reflects well that 1-butanol is the solute that presents the most hydrophobic behavior due to the combined effect of partial dehydration of solvation layers and apolar chain interactions. This effect diminishes as the number of OH groups increases.

In the case of diols, the change in the enthalpic coefficient is related to the relative position of the OH groups. 1,2-Butanediol has the highest coefficient, while 1,3-butanediol and 2,3-butanediol render very similar data and are smaller than the coefficient for 1,4-butanediol. The results with butanediols follow the same trend as shown by propanediols where 1,2-propanediol exhibits a more hydrophobic behavior than 1,3-propanediol [21], and also the behavior reported by Borghesani for 1,2, 1,4 and 1,3-butanediol, but differs in the case of 2,3-butanediol [16]. The pairwise enthalpic coefficient for 1,2-butanediol, when compared with the coefficients of other diols demonstrates that the influence of the alkyl chain, with a larger hydrophobic domain well separated from the hydrophilic groups, improves their promoting effect toward hydrophobic interactions. Probably, a similar situation occurs when the solute considered is 1,4-butanediol. This diol can form intramolecular hydrogen bonds leaving a hydrophobic region well separated from the hydrophilic domain not as large as that for 1,2-butanediol but larger than the hydrophobic domain present in 1,3-butanediol and 2,3-butanediol. These two diols have smaller enthalpic coefficients indicating a reduced overlap of their hydrophobic residues.

This suggests that their behavior is dependent on the accessible surface area and the capacity of forming inter- and intramolecular hydrogen bonds.

The smaller values obtained for the pairwise enthalpic coefficients of 1,2,4-butanetriol and 1,2,3,4-butanetetrol in water is a consequence of the decrease of the hydrophobic domain due to the presence of more OH groups diminishing the influence by their nonpolar interactions and the increase of polar–polar interaction between OH groups that participate in hydrogen-bonding interactions. In the case of 1,2,3,4-butanetetrol, the very low value obtained suggests that apolar chain interactions are almost compensated by polar–polar interaction between OH groups.

Acknowledgements

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