

Polyol – Water Interactions as Reflected by Aqueous Heat Capacity Values

Y.-N. LIAN, A.-T. CHEN, J. SUURKUUSK and I. WADSÖ

Thermochemistry Laboratory, Chemical Center, University of Lund, P.O. Box 740, S-220 07 Lund, Sweden

Aqueous enthalpies of solution have been determined for D-mannitol, D-sorbitol, *meso*-inositol and α -D-glucose. Heat capacities were determined for the pure compounds leading to partial molar heat capacity values for the dilute aqueous solutions.

Heat capacity values for polyols in aqueous solution are discussed in relation to empirical group additivity parameters. It is concluded that the values for sugars and sugar alcohols are significantly higher than expected from the empirical scheme.

A few years ago we reported a simple group additivity scheme for the prediction of partial molar heat capacities of non-ionic compounds in dilute aqueous solutions, $C_{p,2}$.¹ A very good agreement was obtained between experimental and calculated values for hydrocarbons and monosubstituted alkyl compounds such as alcohols, amines, carboxylic acids, amides and ethers. It was also shown that the scheme could be applied to different types of cyclic compounds and that branching of the alkyl chains had only a small influence on the $C_{p,2}$ -values. The results supported the view that solvation effects involving non-ionic groups have the nature of short-range effects.

One important use of such additivity schemes is to detect compounds, or groups of compounds, for which there is a substantial deviation between experimental and calculated values. It is likely that such deviations reflect solute–water interactions which do not exist for the compounds from which the additivity parameters were derived.

It was noted that the scheme predicted quite accurate values for a few simple polyhydroxy compounds, also for those with neighbouring hydroxyl groups. However, a very marked deviation

was noted for sucrose for which the experimental value was found to be more than twice the predicted value, suggesting a specific interaction between sucrose and water.¹ Heat capacity values for other sugars and for sugar alcohols point in the same direction.^{2–5} Specific interactions between polyols and water have also been inferred from other observations such as dielectric and NMR relaxation⁶ and partial molar volumes and compressibilities.^{7–9} Substantial differences have been observed for structurally closely related compounds such as mannitol and sorbitol which differ only in the position of one of their six hydroxyl groups.

In order to describe further the thermodynamic properties of polyols, we report here results from calorimetric measurements on D-mannitol, D-sorbitol, *meso*-inositol and α -D-glucose. Aqueous solution enthalpies have been determined at 288.15, 298.15 and 308.15 K, leading to $\Delta C_{p,2}$ -values for the solution processes. To arrive at $C_{p,2}$ -values [eqn. (1)], heat capacities were also determined for the pure compounds, C_p^* , at 298.15 K.

$$C_{p,2} = \Delta C_{p,2} + C_p^* \quad (1)$$

EXPERIMENTAL

Materials. D-Mannitol was obtained from BDH (organic analytical standard). D-sorbitol, *meso*-inositol and α -D-glucose (anhydrous), of *puriss* quality, were from Fluka. Sorbitol was recrystallized twice from 99.5% ethanol. The other compounds were used without further purification. All samples were dried under vacuum at 80 °C before use in the calorimetric experiments. Reagent-grade water prepared by Milli-Q system was used in the solution calorimetric experiments.

Table 1. Solution calorimetric measurements in water for some polyols. n = number of experiments.

Solute	n	$\Delta H_{\text{sol}}^{\infty} / \text{kJ mol}^{-1}$		n	$T = 298.15$	n	$T = 308.15$	$\Delta C_{\text{p},2}^{\infty} (298.15 \text{ K})$ $\text{J K}^{-1} \text{ mol}^{-1}$
		$T = 288.15$	$T = 298.15$					
D-Mannitol	6	19.88 ± 0.05	7	21.92 ± 0.03	6	24.12 ± 0.07	212 ± 6	
D-Sorbitol	4	17.07 ± 0.03	4	18.66 ± 0.06	5	20.44 ± 0.04	169 ± 5	
meso-Inositol	4	14.21 ± 0.05	5	15.29 ± 0.05	5	16.64 ± 0.02	122 ± 5	
α -D-Glucose	4	9.67 ± 0.01	6	10.88 ± 0.03	6	12.22 ± 0.03	128 ± 3	

Calorimetry. Enthalpy of solution measurements was made with an LKB 8721-1 Precision Calorimeter using a 100 cm³ glass vessel. Electrical calibrations were made for each solution experiment. Small corrections were applied in order to bring the ΔH_{sol} values to the stated temperature (± 0.01 K).

The heat capacity measurements on the pure samples were performed with a micro-drop heat capacity calorimeter.¹⁰ The sample ampoule was charged with *ca.* 0.3 g of material. The ampoules were thermostated at 303 K and were then transferred by free fall to the calorimeter kept at 292 K. The mean temperature in all cases was 298.15 ± 0.03 K. The calorimeter was calibrated with water using the C_{p} -value $75.300 \text{ J K}^{-1} \text{ mol}^{-1}$. For each compound, measurements were made on 4–5 different ampoule fillings. Measurements on each ampoule were repeated *ca.* 5 times.

RESULTS AND DISCUSSION

Final concentrations in the solution calorimetric determinations were in the range of 0.01–0.04 mol dm⁻³. No consistent trend in ΔH -values *versus*

final concentration was observed. Therefore, rather than extrapolating the obtained ΔH -values to zero concentration, average values were calculated and are considered as equal to $\Delta H_{\text{sol}}^{\infty}$. Results are summarized in Table 1. Uncertainties given for $\Delta H_{\text{sol}}^{\infty}$ are twice the standard deviation of the mean.

Sturtevant¹¹ has reported a slightly lower value for the enthalpy of solution of α -D-glucose at 298.15 K, 10.71 kJ mol⁻¹, whereas Taylor and Rowlingson¹² found a slightly higher value, 11.00 kJ mol⁻¹, than that reported here. Sturtevant's value obtained at 308.15 K is in exact agreement with the present result.

Fig. 1 shows a plot of the $\Delta H_{\text{sol}}^{\infty}$ -values *versus* T . A weak curvature is observed and the results for $\Delta H_{\text{sol}}^{\infty}$ were represented by eqns. (2) and (3).

$$\Delta H_{\text{sol}}^{\infty} = a + bT + cT^2 \quad (2)$$

$$\Delta C_{\text{p},\text{sol}}^{\infty} = b + 2cT \quad (3)$$

$\Delta C_{\text{p},\text{sol}}^{\infty}$ -values are given in Table 1. Uncertainties are estimates.

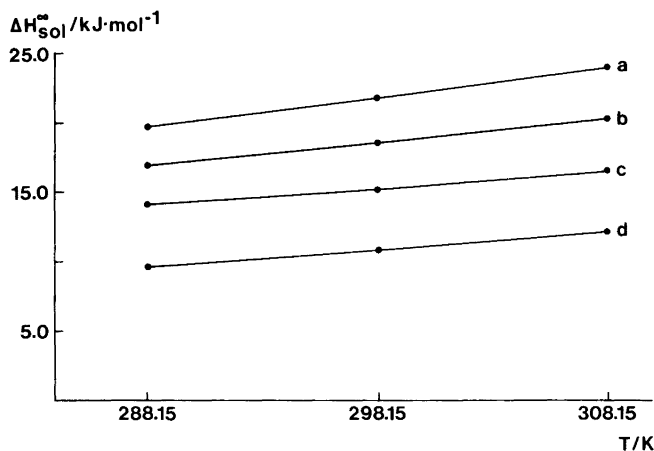


Fig. 1. Enthalpies of solution of some polyols in water. a, D-mannitol; b, D-sorbitol; c, meso-inositol; d, α -D-glucose.

Table 2. Heat capacity values for some polyols.

Compound	$C_p^*/J K^{-1} mol^{-1}$	$C_{p,2}^\infty/J K^{-1} mol^{-1}$
D-Mannitol	239.00 ± 0.16	451 ± 6
D-Sorbitol	241.43 ± 0.31	410 ± 5
meso-Inositol	218.31 ± 0.25	340 ± 5
α -D-Glucose	219.79 ± 0.17	347 ± 3

Results of the heat capacity measurements on the pure samples, C_p^* , and values calculated for the partial molar heat capacities at infinitely dilute aqueous solution, $C_{p,2}^\infty$, are given in Table 2.

Our C_p -value for mannitol is slightly lower than the value which can be derived from the measurements by Spaght *et al.*,¹³ 241 J K⁻¹ mol⁻¹. For glucose, Kawaizumi *et al.*⁴ recently reported the value $C_p = 224 \pm 3$ J K⁻¹ mol⁻¹ at 298.15 K, which is slightly higher than that obtained here.

In aqueous solution α -D-glucose will form an equilibrium mixture of the α and β forms. However,

the main period of the calorimetric solution experiment was short (<2 min), and only a small fraction of the glucose was converted to the β -form (ca. 3% at 298 K). The enthalpy change for glucose mutarotation is small, $\Delta H(\alpha \rightarrow \beta) = -1.16$ kJ mol⁻¹ at 298.15 K¹¹ and we therefore consider the enthalpy and heat capacity values reported here for glucose as referring to the pure α -form.

Table 3 summarizes aqueous $C_{p,2}^\infty$ -values for some sugar alcohols and sugars. In the table, values are also given which were predicted by our additivity scheme¹ and the corresponding deviations (Δ) from the experimental values. In the last column a value expressing the relative deviation from the experimental value is given, $\Delta_{rel} = [\Delta/C_{p,2}^\infty(\text{exp})] \times 100$. Pentoses and hexoses are considered as cyclic compounds¹⁴ and the cyclization parameter¹ of -20 J K⁻¹ mol⁻¹ was added to the value calculated from the group parameters. For the disaccharides and for the trisaccharide, -40 and -60 J K⁻¹ mol⁻¹, respectively, were added. These latter values

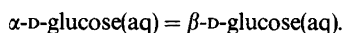
Table 3. Partial molar heat capacities for some polyols in aqueous solution at 298.15 K.

Compound	$C_{p,2}^\infty/J K^{-1} mol^{-1}$				$\Delta^c / J K^{-1} mol^{-1}$	Δ_{rel}^c
	This work	Literature	Preferred value ^a	Calc. value ^b		
Ethanediol		193, ^d 192, ^e 195 ^f	193 ± 2	198	-5	-3
Glycerol		279, ^g 226, ^g 240 ^f	240 ± 4	230	10	4
meso-Erythriol		310 ^f	310 ± 2	262	48	15
D-Xylitol		346 ^f	346 ± 2	294	52	15
D-Arabitol		375 ^f	375 ± 2	294	81	22
L-Arabitol		373 ^f	373 ± 2	294	79	21
Ribitol		376 ^f	376 ± 2	294	82	22
D-Xylose		281 ^h	281 ± 2	141	140	50
D-Ribose		271 ^h	271 ± 2	141	130	48
D-Arabinose		278 ^h	278 ± 3	141	137	49
L-Arabinose		270 ^h	270 ± 4	141	129	48
D-Mannitol	451	455, ^f 440, ⁱ 441 ^j	452 ± 4	326	126	28
D-Sorbitol	410	423, ^f 413 ^j	412 ± 5	326	86	21
meso-Inositol	340		340 ± 5	172	168	49
α -D-Glucose	347	323, ^{j,l} 331 ^{k,l}	347 ± 3	173	174	50
Fructose		352 ^k	352 ± 8	173	179	51
Galactose		324 ^k	324 ± 10	173	151	47
Mannose		337 ^k	337 ± 5	173	164	49
Lactose		619 ^k	619 ± 16	271	348	56
Maltose		614 ^k	614 ± 20	271	343	56
Sucrose		649, ^f 655 ^m	650 ± 2	271	379	58
Raffinose		931 ^k	931 ± 7	369	562	60

^aUncertainties are estimates or were taken from the references indicated. ^bCalculated from group parameter scheme.¹ ^c $\Delta = C_{p,2}^\infty(\text{exp}) - C_{p,2}^\infty(\text{calc.})$. $\Delta_{rel} = [\Delta/C_{p,2}^\infty(\text{exp})] \times 100$. ^dRef. 15. ^eRef. 16. ^fRef. 3. ^gCalculated from ΔC_p values given in Ref. 17, cf. Ref. 1. ^hRef. 5. ⁱRef. 18. ^jCalculated from data in Ref. 2. ^k α, β equilibrium mixture. ^lRef. 4. ^mRef. 19.

are considered as very uncertain but on a relative basis the cyclization parameters will influence the differences between experimental and calculated values (Δ_{rel}) to only a small extent. For instance, if the cyclization parameter for raffinose is neglected, Δ_{rel} will be 54 rather than 60.

The present $C_{p,2}^{\infty}$ -value for mannitol is in excellent agreement with that reported by Di Paola and Bellau,³ whereas their value for sorbitol is higher than the present result. For this substance our value agrees with that derived from the measurements by Bonner and Cerutti.² For glucose the present value is significantly higher than those obtained from heat capacity measurements on glucose solutions, which presumably were α,β equilibrium mixtures. From Sturtevant's mutarotation studies¹¹ the value $\Delta C_p = -9 \text{ J K}^{-1} \text{ mol}^{-1}$ can be derived for the process



Thus, the $C_{p,2}^{\infty}$ -values obtained for the equilibrium mixture (37% α form)²⁰ should be increased by $5 \text{ J K}^{-1} \text{ mol}^{-1}$ in order to refer to the pure α -form, which will somewhat decrease the difference between the earlier and the present results.

The $\Delta C_{p,2}^{\infty}$ -values (Table 1) are all large and positive, suggesting a substantial interaction with the water, as has been pointed out in earlier studies.²⁻⁵ However, we do not consider the ΔC_p -values well-suited for comparison of solute-solvent interactions, as they also will reflect properties of the crystalline compounds. We therefore rather chose to compare the differences between experimental $C_{p,2}^{\infty}$ -values and values predicted from our group-parameter scheme, cf. recent work by Kawaizumi *et al.*^{4,5}

From Table 3 it can be seen that the agreement between predicted and experimental values for ethylene glycol and glycerol is good, which suggests that the presence of neighbouring hydroxyl groups in itself does not impair the additivity scheme. However, for the C_4-C_6 sugar alcohols and for the sugars listed in Table 1, Δ -values are all large. As might be expected, the deviations increase with the size of the solute molecules, but it is interesting to note that there is also a marked relative increase, Δ_{rel} . We note that Δ_{rel} is substantially larger for the pentoses than for the C_5 straight-chain alcohols. The situation is similar for corresponding series of C_6 compounds.

Further, it is interesting to note that the Δ_{rel} -value for the cyclic hexahydroxyl compound *meso*-inositol

is much larger than the Δ_{rel} -values for the corresponding open-chain hexahydroxyl compounds mannitol and sorbitol. The value for *meso*-inositol is, in fact, the same as those found for the (cyclic) pentoses and hexoses.

The Δ_{rel} -values for the disaccharides and the trisaccharide are higher than those for the pentoses and the hexoses, but with the uncertain cyclization parameter in mind we do not consider the difference significant. In summary, it seems as if the high $C_{p,2}^{\infty}$ -values are partly due to a cooperative effect and that the ring structures give significant contributions. We interpret the observed positive Δ -values as caused by endothermic "melting" processes taking place when extensive interactions (hydrogen bonding) between solutes and water decrease with increasing temperature.

Large negative values for ΔC_p in binding reactions involving *e.g.* proteins are often taken as a sign of hydrophobic interactions. The large $C_{p,2}^{\infty}$ -values for polyols suggest that binding reactions involving sugar moieties being transferred from aqueous solution into a water deficient binding site possibly are also characterized by a negative ΔC_p -value.

Acknowledgements. This work has been supported by the Swedish Natural Science Research Council. We gratefully acknowledge the technical assistance of Mrs. G. Gränz.

REFERENCES

- Nichols, N., Sköld, R., Spink, C., Suurkuusk, J. and Wadsö, I. *J. Chem. Thermodyn.* 8 (1976) 1081.
- Bonner, O. D. and Cerutti, P. J. *J. Chem. Thermodyn.* 8 (1976) 105.
- DiPaola, G. and Belleau, B. *Can. J. Chem.* 55 (1977) 3825.
- Kawaizumi, F., Nishio, N., Nomura, H. and Miyahara, Y. *J. Chem. Thermodyn.* 13 (1981) 89.
- Kawaizumi, F., Kushida, S. and Miyahara, Y. *Bull. Chem. Soc. Jpn.* 54 (1981) 2282.
- Tait, M. J., Suggett, A., Franks, F., Ablett, S. and Quickenden, P. A. *J. Solution Chem.* 1 (1972) 131.
- Franks, F., Ravenhill, J. R. and Reid, D. S. *J. Solution Chem.* 1 (1971) 3.
- Høiland, H. and Holick, H. *J. Solution Chem.* 7 (1978) 587.
- Shahidi, F., Farrel, P. G. and Edward, J. T. *J. Solution Chem.* 5 (1976) 807.
- Suurkuusk, J. and Wadsö, I. *J. Chem. Thermodyn.* 6 (1974) 667.

11. Sturtevant, J. M. *J. Phys. Chem.* 45 (1941) 127.
12. Taylor, J. B. and Wawlingson, J. S. *Trans. Faraday Soc.* 51 (1955) 1183.
13. Spaght, M. E., Thomas, S. B. and Parker, G. S. *J. Phys. Chem.* 36 (1932) 882.
14. Angyal, S. J. *Angew. Chem.* 81 (1969) 172.
15. Nichols, N., Sköld, R., Spink, C. and Wadsö, I. *J. Chem. Thermodyn.* 8 (1976) 993.
16. Jolicouer, C. and Lacroix, G. *Can. J. Chem.* 54 (1976) 624.
17. Franks, F., Reid, D. S. and Suggett, A. *J. Solution Chem.* 2 (1973) 99.
18. White, C. M. *J. Am. Chem. Soc.* 58 (1936) 1620.
19. Gucker, F. T., Jr., Pickard, H. B. and Plenck, R. W. *J. Am. Chem. Soc.* 61 (1939) 459.
20. Dawson, R. M., Elliott, D. C., Elliott, W. H. and Jones, K. M. *Data for Biochemical Research*, 2nd Ed., Oxford Univ. Press, London 1969, p. 233.

Received January 29, 1982.