

## THE ENTHALPY OF DILUTION OF AQUEOUS CELLOBIOSE SOLUTIONS AT 298.15 K

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### ABSTRACT

Enthalpy of dilution data for aqueous solutions of cellobiose in water at 25°C are reported and the results obtained are compared with some recent free energy data (T.M. Herrington et al., *J. Chem. Soc., Faraday Trans. 1*, 79 (1983) 845). The free energetic and enthalpic pairwise interaction coefficients obtained from the experimental results have been transposed to the McMillan–Mayer (MM) state to reflect better molecular events. Application of a simplified model for the potential of mean force between solute species leads to the conclusion that there are solute–solute attractions occurring in solution but that these are weak and sensitive to temperature.

### INTRODUCTION

In the last few years there have been numerous studies on the interaction of saccharides, both simple and more complex, with the solvent water. Most of the investigations [1–12] have been directed towards the elucidation of information relevant to the situation in which the solute considered is “infinitely dilute” in the solvent and where solute–solute interactions are absent. While such studies are important in their own right, if attention is directed towards the use of small or model systems to give insight into the behaviour of biological systems, the more important area is not the effectively infinite dilute state but rather the finite concentration region. The interactions which occur under such conditions, even for single solutes, will be necessarily complex since they depend on the interplay of solute–solute, solute–solvent and solvent–solvent interactions. Some progress has been made lately [13–25] in the establishment of empirical rules for the thermodynamic behaviour of solutions containing polyfunctional solutes at finite concentrations. It is however fair to say that these rules are relatively crude and have a somewhat uncertain theoretical base [16,25–27]. They do however have considerable practical utility.

In this paper we report on a microcalorimetric investigation of the enthalpy of dilution of the disaccharide cellobiose [(4-*O*- $\beta$ -D-glucopy-

ranosyl)-D-glucopyranose] in water at 298.15 K. Our principal reason for investigating this system stems from our interest [28] in the interactions occurring between saccharides with naturally occurring polyphenolic substances. However, the information we have obtained here complements some recent work [29] on the excess free energies and volumetric properties of aqueous solutions containing cellobiose.

## EXPERIMENTAL

The cellobiose used was obtained from Fluka and was of Puriss grade. It was dried carefully before use.

The apparatus and procedures used for the determination of the enthalpies of dilution have been described elsewhere [24,30,31].

## RESULTS

The experiments were performed by diluting a solution containing  $n$  moles of cellobiose and of molality  $m$ , with water to give a solution of final molality  $m'$ . The enthalpy change for such a dilution is represented by  $q$  and the primary experimental data are presented in Table 1.

The data were analysed using a procedure based upon the excess thermodynamic functions treatment [32–35]. The excess enthalpy ( $H^{ex}$ ) of a solution containing 1 kg of solvent and a non-electrolytic solute A at molality  $m$

TABLE 1

Experimental enthalpy of dilution results for cellobiose solutions at 298.15 K

$10^4 n$ (mol)	$m$ (mol kg <sup>-1</sup> )	$m'$ (mol kg <sup>-1</sup> )	$-10^3 q$ (J)	$10^3 \Delta$ (J)
5.847	0.2998	0.1527	58.8	0.5
5.415	0.2998	0.0940	80.6	-3.8
11.205	0.2998	0.1964	83.2	-3.4
2.589	0.2998	0.0534	45.1	-1.1
7.412	0.2998	0.1890	55.6	1.0
17.193	0.4939	0.3168	203.1	6.7
17.543	0.4939	0.3187	214.4	-2.6
8.623	0.4939	0.1501	207.6	-3.4
18.024	0.4939	0.3927	125.0	0.7
7.511	0.2010	0.1313	38.2	-2.1
3.794	0.2010	0.0970	27.1	0.1
2.192	0.2010	0.0449	25.3	-1.7
5.574	0.4495	0.1073	131.9	-0.5
15.761	0.4495	0.2886	173.3	1.4
8.277	0.4495	0.2195	129.6	1.6

may be expressed as a polynomial in this molality

$$H^{\text{ex}} = h_{\text{AA}}m^2 + h_{\text{AAA}}m^3 + \dots \quad (1)$$

where  $h_{i,j,k}$  represents, at least notionally, the interactions occurring between the subscripted species. Application of eqn. (1) to the present results gives [22,24] the following expression

$$q = n(m' - m)[h_{\text{AA}} + h_{\text{AAA}}(m' + m) + \dots] \quad (2)$$

and the data were fitted to this using a least-squares routine. It was found that, for the molality range investigated, only the pairwise interaction term was required and the value obtained for this was  $h_{\text{AA}} = 689.1 \pm 8.1 \text{ J kg mol}^{-2}$ , where the error corresponds to the 95% confidence limit. In Table 1.  $\Delta$  is the difference between the experimental and calculated enthalpy of dilution.

## DISCUSSION

In their study of the excess free energies of aqueous cellobiose solutions, Herrington et al. [29] obtained results at the freezing temperature and at 298 K. The expression, corresponding to eqn. (1), for the excess free energy ( $G^{\text{ex}}$ )

$$G^{\text{ex}} = g_{\text{AA}}m^2 + g_{\text{AAA}}m^3 + \dots \quad (3)$$

where  $g_{i,j,k}$  is the free energy analogue of  $h_{i,j,k}$ , can be transposed to give the following expressions for the molal activity ( $\gamma$ ) and osmotic ( $\phi$ ) coefficients.

$$\ln \gamma = (2g_{\text{AA}}m + 3g_{\text{AAA}}m^2 + \dots)/RT \quad (4)$$

$$\phi = 1 + (g_{\text{AA}}m + 2g_{\text{AAA}}m^2 + \dots)/RT \quad (5)$$

Consequently from the earlier data we obtain the following values for the free energy pairwise interaction coefficients

$$273.15 \text{ K: } g_{\text{AA}} = 371 \text{ J kg mol}^{-2}$$

$$298.15 \text{ K: } g_{\text{AA}} = 138 \text{ J kg mol}^{-2}$$

Using these and neglecting heat capacity of dilution contributions we calculate, using the Gibbs–Helmholtz equation, that the pairwise enthalpy coefficient should be  $2711 \text{ J kg mol}^{-2}$  which is very different from the value obtained by direct experiment. No experimental data are available for the excess heat capacities of cellobiose solutions but to bring the experimental enthalpy coefficients into accord with that predicted from the excess free energy measurements, a value of  $-173 \text{ J kg mol}^{-2} \text{ K}^{-1}$  would be required for the pairwise heat capacity coefficient. This is much too large to be realistic given that for sucrose which has the same molar mass, the corresponding value [36] is approximately  $5 \text{ J kg mol}^{-2} \text{ K}^{-1}$ . It seems, therefore,

that there are some errors in the experimental osmotic coefficient data of cellobiose solutions. The errors need not be too large since it is generally found [35] that the determination of enthalpic terms from the temperature variation of free energy terms is very sensitive to the precision of the latter. Our experience [37,38] of both cryoscopic and vapour pressure measurements, using approaches similar to those used by Herrington and her co-workers, leads us to the opinion that results obtained using the cryoscopic technique are generally more reliable and accurate. In view of this we have calculated a value of the free energy coefficient for cellobiose solutions at 298 K assuming the value obtained at the freezing temperature is correct and using the present enthalpy coefficient and the heat capacity term for sucrose. The value obtained using these assumptions if  $g_{AA} = 347 \text{ J kg mol}^{-2}$  and we shall use this in the later discussions.

One feature of the experimentally derived results for pairwise interaction coefficients which has been commented on elsewhere [15,33,39,40] is the fact that care must be taken when attempting to relate them to molecular events. It has been known for some time that the coefficients which are obtained from measurements performed under usual laboratory conditions (these have been termed Lewis–Randall (LR) coefficients [41]) are not a direct measure of molecular interactions and that a closer link exists between such interactions and the McMillan–Mayer (MM) coefficients [33,37,41–46]. Analogous to eqns. (3) and (1) we may write

$$A^{\text{ex}} = a_{AA}c^2 + a_{AAA}c^3 + \dots \quad (6)$$

$$U^{\text{ex}} = u_{AA}c^2 + u_{AAA}c^3 \dots \quad (7)$$

where  $A^{\text{ex}}$  and  $U^{\text{ex}}$  are, respectively, the excess Helmholtz free energy and excess internal energy of a system of unit volume containing a solute of molarity  $c$ , under conditions of constant temperature and where the solution is under a pressure equal to its osmotic pressure. The coefficients  $a_{AA}$  and  $u_{AA}$  are the MM analogues of  $g_{AA}$  and  $h_{AA}$ . These are related to molecular events by the relationships

$$a_{AA}/RT = 2\pi L \int_0^\infty \langle 1 - \exp - [w_{AA}(r)/kT] \rangle r^2 dr \quad (8)$$

and

$$\begin{aligned} u_{AA}/R &= d(a_{AA}/RT)/dT^{-1} \\ &= 2\pi L \int_0^\infty \{ d\langle 1 - \exp - [w_{AA}(r)/kT] \rangle /dT^{-1} \} r^2 dr \end{aligned} \quad (9)$$

where  $w_{AA}(r)$  is the potential of mean force between two solute molecules separated by a distance  $r$  in the pure solvent and the brackets ( $\langle \rangle$ ) denote that orientational averaging is to be performed.

The experimentally derived LR coefficients can be transposed to these MM coefficients in a fairly straightforward way [33,41,44,45]. The required

expressions are

$$a_{AA} = (g_{AA}V_1^0/M_1) + RT[V_A^\ominus - (RTK/2)] \quad (10)$$

and

$$u_{AA} = [d(V_1^\ominus/T)/dT^{-1}](g_{AA}/M_1) + (h_{AA}V_1^0/M_1) - RT^2(dV_A^\ominus/dT) + (R^2T^2K/2) \quad (11)$$

In these equations  $V_1^0$ ,  $M_1$  and  $K$  are, respectively, the molar volume, relative molar mass and compressibility of the pure solvent, and  $V_A^\ominus$  is the partial molar volume at infinite dilution of the solute. In eqn. (11) we have neglected any changes in solvent compressibility with temperature. The MM coefficients were obtained using these relationships and the appropriate volumetric data for the solute [29] and the solvent [47]. The values obtained were:  $a_{AA} = 871 \text{ J dm}^3 \text{ mol}^{-2}$  and  $u_{AA} = 888 \text{ J dm}^3 \text{ mol}^{-2}$ .

Consequently the general conclusions regarding the signs of the MM coefficients appear to be the same as may be drawn from the LR coefficients, i.e., both are positive and apparently reflect some nett repulsion between cellobiose molecules when present as solutes in water. However, it must be stressed that when one considers the sign of the MM free energy coefficient one must not assume too readily that there are no attractive interactions occurring between the solutes. It is clear from eqn. (8) that a zero value for  $a_{AA}$  would result if the potential of mean force between solute species is zero for all values of inter-solute separations. However, simply because in any real system, if the solutes approach each other close enough, closed electron shell repulsions must necessarily occur, i.e., there will be a region of space where  $w_{AA}(r)$  will become large and positive. The result of this is that even in the absence of any attractive contributions,  $a_{AA}$  will become positive and its magnitude, at least to a first approximation, will depend simply on the size of the solute species. The consequence of this is that when one is assessing whether attractions are occurring between solute species in a solvent, it is necessary to subtract from the experimentally derived MM free energy coefficient, the contribution from short-range repulsive interactions. To do this precisely is prohibitively difficult at the present time and it is usual [29,33,44] to approximate the short-range repulsive term by assuming that the solute is a "hard body" of known or assumed shape. Efforts have been made [48] to use more realistic repulsive potentials for some simple solutes but given the present state of our knowledge we are not able to attempt this for polyfunctional solutes such as that considered here. Accordingly, the MM free energy coefficient is given by

$$a_{AA} = a_{AA}(\text{HB}) + a_{AA}(\text{ATT}) \quad (12)$$

where the hard-body contribution is represented by the first term on the r.h.s. of eqn. (12) and the attractive (or indeed repulsive) contribution arising from non-hard-body interactions is the second term.

In their investigation of cellobiose solutions, Herrington et al. [29] approximated the solute as a hard prolate ellipsoid with its semi-axes obtained from molecular models and, using previously derived [49,50] analytical relationships, evaluated the hard-body contribution. Using our terminology the value obtained for this was  $1542 \text{ J dm}^3 \text{ mol}^{-2}$  and putting this in eqn. (12) with the earlier nett MM free energy coefficient, the attractive contribution  $a_{AA}(\text{ATT})$  to the cellobiose–cellobiose interaction is  $-671 \text{ J dm}^3 \text{ mol}^{-2}$ . This represents a significant attraction between cellobiose molecules in water. One can reach similar conclusions about other saccharides and we disagree with the conclusion [51], based on LR coefficients, that there are repulsive “chemical” interactions between such solutes. The *apparent* repulsion is simply a consequence of the reference state used and the misleading conclusions which can be drawn from a common definition of ideality for all solutes. If we direct our attention to the attractive component of eqn. (12) then using this with eqn. (8) gives

$$a_{AA}(\text{ATT})/RT = 2\pi L \int_{\text{HB}}^{\infty} \langle 1 - \exp - [w_{AA}(r)/kT] \rangle r^2 dr \quad (13)$$

where the lower limit of the integral corresponds to some distance specifying the size of the presumed hard body. The internal energy component can be related to this in a simple way by assuming that the hard-body term is independent of temperature so that

$$u_{AA}(\text{ATT})/R = u_{AA}/R = 2\pi L \int_{\text{HB}}^{\infty} \langle [l_{AA}(r)/R] \exp - [w_{AA}(r)/kT] \rangle r^2 dr \quad (14)$$

where  $l_{AA}(r) = \partial[w_{AA}(r)/T]/\partial T^{-1}$ .

It is worth noting that, at this level of approximation, the actual  $u_{AA}$  term is a direct measure of the attractive component  $u_{AA}(\text{ATT})$ . This arises because the hard-body term in eqn. (12) is essentially an entropic component arising from excluded volume sources.

Evaluation of the potential of mean force terms in eqns. (13) and (14) is not possible from the present information, unless a model is assumed for their radial dependence. For simplicity we continue with the assumption [29] that cellobiose may be represented by a prolate ellipsoid and we further assume that the potential of mean force between two molecules may be represented by a square-well of breadth equal to the diameter of two water molecules (i.e., the co-solvent region of each solute molecule is one water molecule thick). Eqn. (13) then takes the form

$$a_{AA}(\text{ATT})/RT = V_{cs} [1 - \exp - (w_{AA}^0/kT)] \quad (15)$$

in which  $V_{cs}$  is a volumetric term representing the interactive volume of the co-solvent regions and is calculable from the dimensions of the ellipsoid [29] and the assumed diameter of a water molecule ( $3.04 \text{ \AA}$ ) [29] and  $w_{AA}^0$

represents the depth of the potential well. Inserting numerical values gives

$$\begin{aligned}\exp - (w_{AA}^0/kT) &= [1 - a_{AA}(ATT)/RTV_{cs}] \\ &= 1 + 6717(2479 \times 9.31) \\ &= 1.029\end{aligned}$$

which corresponds to a value for  $w_{AA}^0$  of  $-71 \text{ J mol}^{-1}$ . To the same level of approximation eqn. (14) becomes

$$u_{AA}/RT = V_{cs} (l_{AA}^0/kT) \exp - (w_{AA}^0/kT) \quad (16)$$

where  $l_{AA}^0 = d(w_{AA}^0/T)d(1/T)$  and again using numerical values we obtain

$$l_{AA}^0/kT = 888/2479 \times 9.31 \times 1.029 = 0.0374$$

which corresponds to a value for  $l_{AA}^0$  of  $93 \text{ J mol}^{-1}$ .

These calculations are necessarily crude but they do serve to stress an important feature of systems such as that discussed here, namely that the interactions tending to bring solute molecules into proximity with each other are weak and are very sensitive to temperature. This weakness of the forces almost certainly explains the difficulty of observing solute-solute interactions by spectroscopic methods [5,52] since not only are there relatively few of these but also, particularly for saccharides, presumably a considerable part of these interactions will be through solute-solute intermolecular hydrogen bonds and these will not be too dissimilar (at least with regard to their spectroscopic characteristics) to the hydrogen bonds existing between, say, saccharide hydroxyl groups and water molecules.

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