Partial molar heat capacities and volumes of transfer of some saccharides from water to aqueous urea solutions at $T = 298.15$ K

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Apparent molar heat capacities $\langle C_p \rangle$ and volumes $\langle V \rangle$ of seven monosaccharides {D(--)-ribose, D(--)-arabinose, D(+)-xylose, D(+)-glucose, D(+)-mannose, D(+)-galactose, D(--)-fructose}, seven disaccharides {sucrose, D(+)-cellobiose, lactulose, D(+)-melibiose hemihydrate, D(+)-maltose monohydrate, D(+)-lactose monohydrate, D(+)-trehalose dihydrate} and one trisaccharide {D(+)-rafEnose pentahydrate} have been determined in (0.5, 1.0, 1.5, and 3.0) mol $\cdot$ kg$^{-1}$ aqueous urea solutions at $T = 298.15$ K from specific heat and density measurements employing a Picker flow microcalorimeter and a vibrating-tube densimeter, respectively. By combining these data with the earlier reported partial molar heat capacities $C_{p,2}^0$ and volumes $V_2^0$ in water, the corresponding partial molar properties of transfer ($C_{p,2}^0$ and $V_2^0$) from water to aqueous urea solutions at infinite dilution have been estimated. Both the $C_{p,2}^0$ and $V_2^0$ values have been found to be positive for all the sugars and to increase with increase in concentration of the cosolute (urea), suggesting that the overall structural order is enhanced in aqueous urea solutions. This increase in structural order has been attributed to complex formation between sugars and urea molecules through hydrogen bonding and to a decreased effect of urea on water structure. The transfer parameters have been rationalized in terms of solute-cosolute interactions using a cosphere overlap hydration model. Pair, triplet and higher-order interaction coefficients have also been calculated from transfer functions and their sign and magnitude have been discussed.

KEYWORDS: saccharides; heat capacity; volume; interaction coefficients; stereochemical effects
1. Introduction

The hydration characteristics of saccharides\(^1\) to 6\) and their interactions with electrolytes and nonelectrolytes\(^7\) to 15\) in aqueous media are of significant biological and thermodynamic importance. It has been widely reported\(^16\) to 22\) that sugars and polyols act as efficient stabilizing agents for proteins/enzymes because of their ability to enhance the structure of water. Lee and Timasheff\(^17\) attributed the stabilizing effect of sucrose to the positive Gibbs free energy required to form a cavity in the solvent due to an increase in the solvent cohesive force when sucrose was added to water. Bull and Breese\(^23\) suggested that sugars enhanced the structure of water in the immediate neighbourhood of the protein.

On the other hand, urea forms nearly ideal mixtures because of possible compensating interactions with water and can exhibit a chaotropic action on ordered systems such as micelles, folded globular proteins and water soluble synthetic polymers\(^24\) to 25\) It has also been reported that urea enhances the solubility of the nonpolar compounds due to the weakening of hydrophobic interactions, which contribute to the stability of micelles and folded globular proteins and thus deem water of its unique property of promoting hydrophobic interactions\(^26\) Furthermore, it is well known\(^27\) to 30\) that the extent of denaturation of certain proteins by urea-type denaturants is reduced in the presence of sugars or polyhydroxy alcohols. However, the mechanism by which this renaturating effect on protein structure is induced, either by the direct binding of urea with the polyhydroxy compound/protein molecule or through the alteration of water structure, is not clearly understood. Thus the investigation of interactions between urea and saccharides having different stereochemistry will help to clarify the nature and specificity of these interactions.

In continuation of our investigations of the solution behaviour of saccharides, we report here, apparent molar heat capacities \(\bar{C}_p\) and volumes \(\bar{V}\) of various mono-, di- and tri-saccharides in (0.5, 1.0, 1.5 and 3.0) mol \cdot kg\(^{-1}\) aqueous urea solutions at \(T = 298.15\) K. By combining these data with the earlier reported\(^1\) to 8\) partial molar heat capacities \(C^o_p\) and volumes \(V^o\) in water, the corresponding partial molar properties of transfer \((C^o_p)^\text{tr}\) and \(V^\text{tr}\) respectively) at infinite dilution have been determined. These transfer parameters are interpreted in terms of (solute + cosolute) interactions. The effect of cosolute concentration has also been discussed. Coefficients of pair, triplet and higher-order interactions in terms of (solute + cosolute) have also been calculated from transfer functions.

2. Experimental

A picker differential flow microcalorimeter (Sodev Inc., Sherbrooke, Canada) was employed for measuring the heat capacities per unit volume of the solutions. Its operating principle and procedure have been described elsewhere\(^31\) The precision of the microcalorimeter used was \(\pm 0.5\) per cent with a limit of detectability of \(7 \cdot 10^{-5}\) \(\text{J K}^{-1} \cdot \text{g}^{-1}\). A programmable circulating thermostat supplied with the instrument was used to maintain the temperature within \(\pm 1 \cdot 10^{-3}\) K. The current and voltage were measured with accuracies of \(\pm 1 \cdot 10^{-4}\) A and \(\pm 1 \cdot 10^{-3}\) V, respectively using a Systronics digital multimeter. The signals were recorded by using a Bryans-2800 potentiometric strip chart recorder. The specific heat capacity for the reference water at
$T = 298.15\ \text{K}$ was taken\textsuperscript{(31)} as $4.1796\ \text{J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}$. The performance of the calorimeter was checked by measuring the apparent molar heat capacities of aqueous sodium chloride solutions at $T = 298.15\ \text{K}$. A good agreement with the literature was found.\textsuperscript{(31)}

A digital vibrating-tube densimeter (model DMA 60/602, Anton Paar, Austria) was used to measure the densities of the solutions. The details of its principle and operation have been described elsewhere.\textsuperscript{(32)} A Tronac PTC-40 proportional temperature controller and an MK-70 ultracryostat were used to control the temperature of the bath used. The temperature was checked by using an NBS thermometer with an accuracy of $\pm 0.01\ \text{K}$ and the thermal stability of the bath was found to be better than $\pm 1\times 10^{-3}\ \text{K}$. The instrument was calibrated with dry air and water to yield density values accurate to within $\pm 3\times 10^{-6}\ \text{g} \cdot \text{cm}^{-3}$. All the measurements of the densities of the various solutions were made with reference to pure water having a density of $0.997047\ \text{g} \cdot \text{cm}^{-3}$ at $T = 298.15\ \text{K}$.\textsuperscript{(33)} The densities of aqueous sodium chloride solutions were in excellent agreement with the literature values\textsuperscript{(32,34)–37}.

The various saccharides whose mass fraction purities are given in parentheses were purchased from Sigma Chemical Company: D(-)-ribose (0.98), D(-)-arabinose (0.98), D(+)-glucose (0.997), D(-)-fructose (0.98), sucrose (0.995), lactulose (0.98), D(+)-melibiose hemihydrate (0.98) and D(+)-raffinose pentahydrate (0.99). D(+)-xylose, D(+)-mannose, D(+)-galactose, D(+)-cellobiose, D(+)-maltose monohydrate, D(+)--lactose monohydrate and D(+)-trehalose dihydrate were obtained from the American National Institute of Standards and Technology (NIST). Their characterization has been reported elsewhere.\textsuperscript{(35–38)} These sugar samples were used without further purification, however, before use they were dried over P2O5 in a desiccator. Analar grade urea obtained from BDH was used after drying for 48 h at $T = 333\ \text{K}$. All the solutions were prepared using distilled and deionized water obtained by passing double distilled water through a Cole-Parmer ion-exchange resin mixed bed column. The water was then degassed before use. The solutions were made by weight using a Mettler balance with a resolution of 0.01 mg.

3. Results

The apparent molar heat capacity $\langle \delta S \rangle C_P$ and volume $\langle \delta S \rangle V$ of the sugars studied were obtained from the experimentally measured specific heat capacity and density data in (0.5, 1.0, 1.5 and 3.0) mol $\cdot$ dm$^{-3}$ aqueous urea solutions using the following relations:

\[
\langle \delta S \rangle C_P = M \left[ 1000 (c_p^o - c_p)/m \right] \tag{1}
\]

\[
\langle \delta S \rangle PV = (M/p) - \left[ 1000 (p - p_0)/mppl \right] \tag{2}
\]

where $M$ is the molar mass of the solute, $m$ is the molality of the solution, $c_p^o$, $c_p$ and $p_0$, and $p$ are the corresponding specific heat capacities and densities of the solvent and the solution, respectively.

The values of $p$, $c_p$, $\langle \delta S \rangle C_P$ and $\langle \delta S \rangle V$ for the various sugars in the aqueous urea solutions at $T = 298.15\ \text{K}$ as a function of molality are summarized in table 1. At infinite dilution, the partial molar heat capacities $\langle \delta S \rangle C_P^o = C_P^o$ and partial molar volumes $\langle \delta S \rangle V = F_2^o$ were calculated from the corresponding $C_P^o$ and $V$ data by taking the average of all the data
TABLE 1. Densities $\rho$, specific heat capacities $c_p$, apparent molar heat capacities $\bar{c}_p$ and apparent molar volumes $\bar{V}$ of some saccharides in aqueous solutions of urea at $T = 298.15$ K

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<th>$\rho$ (g $\cdot$ cm$^{-3}$)</th>
<th>$c_p$ (J $\cdot$ K$^{-1}$ $\cdot$ g$^{-1}$)</th>
<th>$\bar{c}_p$ (J $\cdot$ K$^{-1}$ $\cdot$ mol$^{-1}$)</th>
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### TABLE 1—continued

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**Lactulose**

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**1.0 mol-kg$^{-1}$ urea solution**

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**D(++)-Melibiose hemihydrate**

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**D(++)-Maltose monohydrate**

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**1.0 mol-kg$^{-1}$ urea solution**

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Heat capacities and volumes of transfer of saccharides

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points where a negligible concentration dependence within the experimental uncertainty was observed. However, in cases where a concentration dependence was observed, these properties were determined by least-squares fits of the corresponding data to the following equations:

\[
\langle S_{\gamma p} \rangle = 4\gamma \frac{c}{c} + sc \cdot m, \quad (3)
\]

\[
\langle PV \rangle = \langle P \rangle \cdot \gamma \frac{c}{c} \cdot sym. \quad (4)
\]
The values of \( s_c \) and \( s_y \), the respective slopes and the \( C^o_{p2} \) and \( F^o_2 \) values for the various sugars in different concentrations of urea are presented in tables 2 and 3 along with their standard deviations. The uncertainties in \( \rho C^o_p \) and \( \rho V \) vary in the range \( \pm(1 \text{ to } 3) \) \( J \cdot K^{-1} \cdot \text{mol}^{-1} \) and \( \pm(0.02 \text{ to } 0.10) \) \( \text{cm}^3 \cdot \text{mol}^{-1} \), respectively.

The partial molar heat capacities of transfer \( C^o_{p,2U} \) and partial molar volumes of transfer \( C^o_{p,2U} \) to aqueous urea solutions have been determined as follows:

\[
C^o_{p,2U}(\text{water} \rightarrow \text{aqueous urea}) = C^o_{p2}(\text{aqueous urea}) - C^o_{p2}(\text{water}), \quad (5)
\]

\[
F^o_2(\text{water} \rightarrow \text{aqueous urea}) = V^o_2(\text{aqueous urea}) - V^o_2(\text{water}). \quad (6)
\]

The transfer parameters are given in tables 2 and 3.

### 4. Discussion

**PARTIAL MOLAR HEAT CAPACITIES OF TRANSFER \( C^o_{p,2U} \)**

The \( C^o_{p,2} \) values for the sugars in aqueous urea solutions are higher than the corresponding values in water resulting in positive heat capacities of transfer (table 2). These values increase systematically with the concentration of urea in all the cases. Very few studies on partial molar heat capacities of sugars in urea solutions are available in the literature. Jasra and Ahluwalia\(^{(11)}\) have reported \( C^o_{p,2} \) values at \( T = 303.15 \text{ K} \) for some saccharides such as D(+-)glucose, sucrose, D(+-)cellobiose and D(+-)maltose monohydrate from enthalpy of solution data at \( T = 298.15 \text{ K} \) and \( T = 308.15 \text{ K} \) and these are: (17, 10, and 42) \( J \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \) for D(+-)glucose; (54, 88, and 100) \( J \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \) for sucrose; (9, 94, and 85) \( J \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \) for D(+-)maltose monohydrate and (13, 30, and 61) \( J \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \) for D(+-)cellobiose in (2, 4, and 6) \text{mol} \cdot \text{kg}^{-1} \text{urea} \) solutions, respectively. The present \( C^o_{p,2} \) value at \( T = 298.15 \text{ K} \) in 3 \text{m} \text{urea}, 80 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \), for sucrose is quite comparable while the values of (87, 112, and 63) \( J \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \) for D(+-)glucose, D(+-)maltose monohydrate and D(+-)cellobiose, respectively are comparatively higher than those reported in the literature\(^{(11)}\). The present values emanating from direct measurements are believed to be more accurate.

A simple examination of the data in table 2 reveals that the \( C^o_{p,2} \) values of the various sugars increase from mono- to di- to trisaccharides, however this trend is not found in the corresponding transfer values. Furthermore, among the monosaccharides it can be seen that the \( C^o_{p,2,U} \) values decrease somewhat from the aldopentoses to aldohexoses and that for a single ketohexose the decrease is quite appreciable. The dependence of the \( C^o_{p,2,U} \) values for various sugars on the concentration of urea is depicted in figure 1. It can be seen that the \( C^o_{p,2,U} \) values for the studied monosaccharides tend to level off except for D(+-)mannose and D(+-)fructose where the increase is almost linear. However, in the case of di- and tri-saccharides the \( C^o_{p,2,U} \) values increase almost linearly except for D(+-)maltose monohydrate and D(+-)melibiose hemihydrate, for which the values tend to level off. These trends indicate that the level of saturation of the interactions of these solutes with urea vary in the different cases.

Significant positive transfer values of heat capacities suggest that the overall structural order is enhanced in aqueous urea solutions. The cosphere overlap model developed
TABLE 2. Partial molar heat capacities \( C_{p,2} \) of some saccharides in water and aqueous urea solutions at infinite dilution along with their corresponding transfer values \( C_{p,2,tr} \); \( m \) represents the molality of urea solutions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Monosaccharides</th>
<th>Water ( m )</th>
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<th>1.0</th>
<th>1.5</th>
<th>3.0</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>3.0</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>m/(mol ( \cdot \text{kg}^{-1} )) &amp; ( \pm ) standard deviation</td>
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<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>D(-)-Ribose</td>
<td></td>
<td></td>
<td>279(2)</td>
<td>300(2)</td>
<td>324(3)</td>
<td>347(3)</td>
<td>377(2)</td>
<td>21</td>
<td>45</td>
<td>68</td>
</tr>
<tr>
<td>D(-)-Arabinose</td>
<td></td>
<td></td>
<td>284(3)</td>
<td>302(2)</td>
<td>324(2)</td>
<td>349(3)</td>
<td>380(2)</td>
<td>18</td>
<td>40</td>
<td>65</td>
</tr>
<tr>
<td>D(+)-Xylose</td>
<td></td>
<td></td>
<td>279(2)</td>
<td>298(2)</td>
<td>323(2)</td>
<td>340(3)</td>
<td>369(2)</td>
<td>19</td>
<td>44</td>
<td>61</td>
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<td></td>
<td>342(2)</td>
<td>365(2)</td>
<td>378(2)</td>
<td>405(3)</td>
<td>429(3)</td>
<td>23</td>
<td>36</td>
<td>63</td>
</tr>
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<td></td>
<td>346(3)</td>
<td>365(2)</td>
<td>379(3)</td>
<td>390(4)</td>
<td>428(3)</td>
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<td>33</td>
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<td>361(2)</td>
<td>381(3)</td>
<td>401(4)</td>
<td>425(3)</td>
<td>16</td>
<td>36</td>
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<tr>
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<td></td>
<td>365(2)</td>
<td>373(3)</td>
<td>385(2)</td>
<td>402(2)</td>
<td>427(2)</td>
<td>8</td>
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<td>37</td>
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</table>

| Disaccharides  |                 |               | 648(3) | 668(3) | 679(2) | 689(3) | 728(4) | 20 | 31 | 41 | 80 |
| D(-)-Cellobiose|                 |               | 665(3) | 675(3) | 683(2) | 692(4) | 728(3) | 10 | 18 | 27 | 63 |
| Lactulose      |                 |               | 663(3) | 681(4) | 697(3) | 718(3) | 66  | 34 | 55 |     |
| D(+)-Melibiose-|                 |               | 660(3) | 726(2) | 741(4) | 758(3) | 66  | 81 | 98 |     |
| hemihydrate    |                 |               |        |        |        |        |      |     |     |     |
| D(+)-Maltose   |                 |               | 694(3) | 740(2) | 760(3) | 770(4) | 806(3) | 46 | 66 | 76 | 112|
| monohydrate    |                 |               |        |        |        |        |      |     |     |     |
| D(+)-Lactose   |                 |               | 729(3) | 751(3) | 764(4) | 776(3) | 823(2) | 22 | 35 | 47 | 94 |
| monohydrate    |                 |               |        |        |        |        |      |     |     |     |
| D(+)-Trehalose |                 |               | 799(3) | 813(3) | 826(4) | 839(3) | 887(4) | 14 | 27 | 40 | 88 |
| dihydrate      |                 |               |        |        |        |        |      |     |     |     |
| D(+)-Raffinose |                 |               | 1337(4) | 1349(3) | 1359(3) | 1371(4) | 1415(2) | 12 | 22 | 34 | 78 |
| pentahydrate   |                 |               |        |        |        |        |      |     |     |     |

Parentheses contain standard deviations.
Uncertainties in \( C_{p,2} \) values range from 3 J \( \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \) to 5 J \( \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \), estimated by taking the square root of the sum of the squares of the standard deviations in aqueous and mixed aqueous solutions.

* Values of \( Sc/\text{unit} \).

\(^{a}\) Reference 6.
TABLE 3. Partial molar volumes $V^\circ$ of some saccharides in water and aqueous urea solutions at infinite dilution along with their corresponding transfer values $V^\circ_{2,\text{tr}}$ at $T = 298.15$ K. $m$ represent the molality of the urea solutions.

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<td>95.74</td>
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</tbody>
</table>
by Gurney\textsuperscript{(39)} is invoked to explain the transfer heat capacity and volume data. The properties of the water molecules in the hydration cosphere depend on the nature of the solute species.\textsuperscript{(40,41)} The region occupied by the solvent that is markedly affected by the presence of the solute molecules is termed the cosphere. According to this model, when two molecules approach each other, their hydration cospheres overlap and some of the cosphere material is displaced resulting in changes in the thermodynamic properties.\textsuperscript{(42,44)} This overlap comes into play because of the following interactions between the saccharide (solute) and urea (cosolute) molecules: the interaction between the hydrophilic urea molecules and the polar/hydrophilic, hydroxy sites of the sugars; and the interaction between the hydrophilic urea molecules and the hydrophobic parts/groups of the sugars. The first type of interaction contributes positively, whereas the second type contributes negatively to $C^\circ_{p, 2H}$ values. The significant positive $C^\circ_{p, 2H}$ values observed for all the sugars suggest\textsuperscript{1} that the hydrophilic-hydrophilic interactions dominate over the hydrophobic-hydrophilic interactions. The increase in $C^\circ_{p, 2H}$ values with increase in concentration of urea, indicates a further strengthening of the hydrophilic-hydrophilic interactions. Since urea can form hydrogen bonds easily both with proton donors and acceptors, and as saccharides contain embedded in them large numbers of potential hydrogen bonding sites, the mutual overlap of the hydration cospheres of urea and sugar molecules will lead to an increase in the magnitude of hydrogen-bonding interactions.

For hydrophobic solutes, negative heat capacities of transfer\textsuperscript{(45-52)} and, positive enthalpies and entropies of transfer\textsuperscript{(47-50,53-55)} from water to aqueous urea solutions have been reported, indicating a net bond breakage and thus an increase in disorder of the solvent.
FIGURE 1. Partial molar heat capacity transfer values $C_{p,2,u}$ against the molality $m$ of urea solutions for some saccharides at $T = 298.15$ K. a, D(--)-ribose; *, D(+)-arabinose; A, D(+)-xylose; O, D(+)-glucose; X, D(+)-galactose. b, *, D(+)-mannose; *, D(--)-fructose. c, *, D(+)-maltose monohydrate; *, D(+)-melibiose hemihydrate. d, *, sucrose; *, D(+)-cellobiose; A, lactulose; x, D(+)-lactose monohydrate; *, D(+)-trehalose dihydrate; *, D(+)-raffinose pentahydrate.

system. On the other hand, the ionic solutes (e.g. alkali metal halides)\(^{(56)}\) are accompanied by positive heat capacities of transfer and, negative enthalpies\(^{(5,51,57)}\) and entropies of transfer from water to aqueous urea solutions which result in a decrease in the disorder of the solvent system and an increase in hydrogen bonding. Similarly, positive $C_{p,2,u}$ values have also been reported\(^{(50)}\) for hydrophilic groups such as the peptide group (-CONH-), and the peptide backbone unit (-CH2CONH-) with potential hydrogen-bonding sites, from water to aqueous urea solutions. Therefore, the significant positive $C_{p,2,u}$ values observed in this work for sugars from water to aqueous urea solutions indicate a behaviour similar to ionic or hydrophilic solutes. This strengthens the view that positive values of $C_{p,2,u}$ in-
Heat capacities and volumes of transfer of saccharides

PARTIAL MOLAR VOLUMES OF TRANSFER $V^o_{\text{m}}$

All the mono-, di- and trisaccharides in aqueous urea solutions (0.5, 1.0, 1.5, and 3.0) mol • kg\(^{-1}\) at $T = 298.15$ K have $F^o_2$ values higher than the corresponding values.
in water and thus exhibit positive $F_{2u}^o$ values which increase with the concentration of the cosolute. Very few studies on partial molar volumes of sugars in urea solutions are available in literature. Sangster et al.\cite{14} have reported some data for sucrose alone and the $V_2^o$ values at $T = 298.15 \text{ K}$ in (0.3214, 0.7037 and 1.4834) mol $\cdot$ kg$^{-1}$ urea solutions are (213.28, 216.87 and 222.25) cm$^3$ $\cdot$ mol$^{-1}$, respectively and thus the $F_{2u}^o$ values range from (1.5 to 10) cm$^3$ $\cdot$ mol$^{-1}$, which are appreciably higher than our values (table 3). There are no other data available for comparison. Positive $V_2^o$ values from water to aqueous urea solutions have also been reported\cite{39, 59-61} for hydrophobic and ionic solutes.

Plots of $F_{2u}^o$ against the molality of urea (figure 2) for the studied saccharides show nonlinear behaviour in the majority of the cases. However, in some cases, such as D(+)-xylose, D(-)-ribose, D(+)-maltose monohydrate, D(+)-lactose monohydrate, D(+)trehalose dihydrate, and D(+)-melibiose hemihydrate, the $F_{2u}^o$ values tend to level off with urea concentration. This trend, as in the $C_{2u}^o$ values, certainly arises from multiple contributions.

Franks et al\cite{62} have reported that the partial molar volume at infinite dilution of a nonelectrolyte is made up of an intrinsic molar volume $F_v$ of the non-hydrated solute and a contribution due to the interaction of the solute with water, $V_r$:

$$V_2^o = V_{mi} + V_r$$ (7)

Some investigators\cite{63, 64} have suggested that $V_{mi}$ is made up of two types of contributions.

$$V_{mi} = V_{v,w} + \chi_{void}$$ (8)

where $F_{v,w}$ is the van der Waals volume and $F_{void}$ is the associated void or empty volume.\cite{65, 66}

Shahidi et al\cite{67} have modified this equation to find the contribution of one molecule towards the partial molar volume of a hydrophilic solute as follows:

$$V_{%} = F_{v,w} + \chi_{void} - n\alpha_s$$ (9)

where $\alpha_s$ is the shrinkage in volume caused by interaction of hydrogen bonding groups with water molecules, and $n$ is the potential number of hydrogen bonding sites in a molecule. Therefore, the partial molar volume of a sugar molecule can be represented as,

$$F_2^o = F_{v,w} - \chi_{void} - \chi_{shrinkage}$$ (10)

If one assumes that $F_{v,w}$ and $F_{void}$ have the same magnitudes in water and aqueous urea solutions, the positive volume change accompanying the transfer of sugars from water to an aqueous urea solution may result from a decrease in the shrinkage in volume $\chi_{shrinkage}$ because of interactions between urea and -OH groups of sugars. The interaction of urea with sugars diminishes further the structure breaking effect of urea on water. In other words, more water is released as bulk water in the presence of sugars. Since bulk water has a higher volume contribution\cite{68} than broken structure water, this factor may therefore contribute positively to the $F_{2u}^o$ values. Another way to express the solute-cosolute interactions is through the csphere overlap model, where hydrophilic-hydrophilic type interactions contribute positively and hydrophobic-hydrophilic negatively to $F_{2u}^o$.\cite{69, 70, 71}
Heat capacities and volumes of transfer of saccharides

values\(^{39,42}\). The positive $F_2^{o,u}$ values obtained in this work (table 3) for all the sugars suggest that the former type of interactions dominates over the latter and the $C_2^{o,p}$ values support this observation.

Sangster et al.\(^{14}\) have attributed the positive $F_2^{o,u}$ values for sucrose from water to an aqueous urea solution to dehydration of sucrose in the mixed solvent and to decreased sucrose-sucrose interactions, reflected in the depressed $\Delta f V$ against $m$ slope. These two observations lead to a corresponding increase in the interactions between the solute and cosolute that provide the dominant contributions to the transfer parameters.

**INTERACTION COEFFICIENTS**

Kozak et al.\(^{69}\) have proposed a theory based on the McMillan-Mayer\(^{70}\) theory of solutions which permits the formal separation of the effects due to interactions between pairs of solute molecules and those due to interactions involving three or more molecules. Friedmann and Krishna\(^{40}\) and Franks et al.\(^{41}\) have further included solute-cosolute interactions in the solvation spheres. Various workers\(^{71-73}\) have used the theory to study solute-cosolute interactions in aqueous media. According to this treatment, a thermodynamic transfer function at infinite dilution ($\gamma^o$) can be expressed as:

$$F_2^{o,u}(\text{water} \rightarrow \text{aqueous urea}) = 2\gamma^{AB} + \gamma^{ABB} + \gamma^{ABBB}$$

where $A$ stands for saccharide and $B$ stands for urea, and $m$ is the molality of urea (cosolute), and $\gamma^{AB}$, $\gamma^{ABB}$ and $\gamma^{ABBB}$ are pair, triplet and quartet intermolecular interaction coefficients. The corresponding parameters, namely $CAB$, $CABB$, $CABBB$ for the heat capacities and $DAB$, $UABB$, $UABBB$ for the volumes determined from the $C_2^{o,p}$ and $F_2^{o,u}$ values are summarized in table 4.

The pair interaction coefficient $CAB$ is positive for all the saccharides. For monosaccharides the values range from (13 to 22) J • K\(^{-1}\) • mol\(^{-1}\) • (mol • kg\(^{-1}\))\(^{-1}\) with an exceptionally low value for D(+)-fructose (3 J • K\(^{-1}\) • mol\(^{-1}\) • (mol • kg\(^{-1}\))\(^{-1}\) ). For di- and trisaccharides the CAB values are almost of the same order (11 to 26) J • K\(^{-1}\) • mol\(^{-1}\) • (mol • kg\(^{-1}\))\(^{-1}\) as those of monosaccharides except for D(+)-melibiose hemihydrate and D(+) maltose monohydrate for which the values are exceptionally high: (109 and 60) J • K\(^{-1}\) • mol\(^{-1}\) • (mol • kg\(^{-1}\))\(^{-1}\), respectively. The CABB values are positive for monosaccharides except for D(+) mannose and negative for disaccharides which indicates that in the case of monosaccharides triplet interactions enhance the structural order whereas the reverse is true in the case of disaccharides. From the signs of the CABBB values, it can be seen that quartet interactions in mono- and disaccharides are opposite to the corresponding triplet interactions. Large positive CAB values suggest that due to the overlap of hydration spheres of the saccharides and urea molecules strong interactions are occurring between them, most probably through hydrogen bonding. This is in line with the conclusion drawn from the cosphere overlap model in the previous section.

The DAB values are also positive for all the saccharides except for sucrose. The UABB values are negative and those of UABBB are positive in all the cases with few exceptions; this is not in line with the trends observed in the corresponding interaction coefficients of the heat capacity data. Large positive DAB values indicate an increase in volume as
TABLE 4. Interaction coefficients \( C_{AB} \), \( C_{ABB} \), \( \gamma_{AB} \), \( \gamma_{ABB} \) and \( \gamma_{ABBB} \) of some sugars in aqueous urea solutions calculated by using equation (11) at \( T = 298.15 \) K

<table>
<thead>
<tr>
<th>Compound</th>
<th>( C_{AB} ) ( \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} )</th>
<th>( C_{ABB} ) ( \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-2} )</th>
<th>( C_{ABB} ) ( \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} )</th>
<th>( \gamma_{AB} ) ( \text{cm}^3 \cdot \text{mol}^{-1} )</th>
<th>( \gamma_{ABB} ) ( \text{cm}^3 \cdot \text{mol}^{-1} )</th>
<th>( \gamma_{ABBB} ) ( \text{cm}^3 \cdot \text{mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Monosaccharides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D(-)-Ribose</td>
<td>18</td>
<td>4.2</td>
<td>-1.17</td>
<td>0.57</td>
<td>-0.24</td>
<td>0.035</td>
</tr>
<tr>
<td>D(—)-Arabinose</td>
<td>13</td>
<td>6.9</td>
<td>-1.56</td>
<td>0.23</td>
<td>-0.13</td>
<td>0.043</td>
</tr>
<tr>
<td>D(+)-Xylose</td>
<td>19</td>
<td>2.0</td>
<td>-0.76</td>
<td>0.16</td>
<td>0.05</td>
<td>-0.012</td>
</tr>
<tr>
<td>D(+)Glucose</td>
<td>17</td>
<td>3.3</td>
<td>-0.97</td>
<td>0.60</td>
<td>-0.29</td>
<td>0.063</td>
</tr>
<tr>
<td>D(+)Mannose</td>
<td>22</td>
<td>-4.9</td>
<td>0.74</td>
<td>0.23</td>
<td>-0.10</td>
<td>0.026</td>
</tr>
<tr>
<td>D(+)Galactose</td>
<td>13</td>
<td>5.0</td>
<td>-1.22</td>
<td>0.65</td>
<td>-0.33</td>
<td>0.068</td>
</tr>
<tr>
<td>D(—)-Fructose</td>
<td>3</td>
<td>6.5</td>
<td>-1.22</td>
<td>0.41</td>
<td>-0.17</td>
<td>0.030</td>
</tr>
<tr>
<td><strong>Disaccharides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sucrose</td>
<td>24</td>
<td>-6.9</td>
<td>1.14</td>
<td>-0.10</td>
<td>0.31</td>
<td>-0.050</td>
</tr>
<tr>
<td>D(+)-Cellobiose</td>
<td>11</td>
<td>-1.5</td>
<td>0.36</td>
<td>0.73</td>
<td>-0.12</td>
<td>0.015</td>
</tr>
<tr>
<td>Lactulose</td>
<td>21</td>
<td>-6.0</td>
<td>2.33</td>
<td>1.67</td>
<td>-1.41</td>
<td>0.453</td>
</tr>
<tr>
<td>D(+)Melibiose hemihydrate</td>
<td>109</td>
<td>-69.3</td>
<td>17.67</td>
<td>11.38</td>
<td>-8.17</td>
<td>2.120</td>
</tr>
<tr>
<td>D(+)-Maltose monohydrate</td>
<td>60</td>
<td>-21.6</td>
<td>3.12</td>
<td>0.78</td>
<td>-0.05</td>
<td>-0.006</td>
</tr>
<tr>
<td>D(+)-Lactose monohydrate</td>
<td>26</td>
<td>-7.0</td>
<td>1.18</td>
<td>1.06</td>
<td>-0.32</td>
<td>0.041</td>
</tr>
<tr>
<td>D(+)-Trehalose dihydrate</td>
<td>15</td>
<td>-1.3</td>
<td>0.31</td>
<td>2.06</td>
<td>-0.87</td>
<td>0.129</td>
</tr>
<tr>
<td><strong>Trisaccharide</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D(+)-Raffinose pentahydrate</td>
<td>12</td>
<td>-1.0</td>
<td>0.30</td>
<td>1.58</td>
<td>-0.53</td>
<td>0.087</td>
</tr>
</tbody>
</table>
the hydrogen-bonding interactions take place between saccharides and urea and this again supports the view that hydrophilic-hydrophilic interactions dominate over the others. The relative weightings of the various coefficients may also be judged from their contributions to transfer parameters at different molalities of urea by plotting these contributions against the concentration of urea. It has been observed that up to 1.0 mol • kg$^{-1}$ urea transfer parameters arise mainly from pair solute-cosolute interactions in almost all the cases and triplet and quartet type interactions contribute effectively only at urea molalities higher than 1.0 mol • kg$^{-1}$. The interaction coefficients derived from the heat capacity and volumes data have almost similar trends for disaccharides but this is not the case for the monosaccharides. However, more data are required at more concentrations of urea to confirm this trend.

STEREOCHEMICAL EFFECTS

Various experimental as well as theoretical attempts are underway to explore the correlation between the hydration characteristics of saccharides and their stereochemistry. The hydration of carbohydrates has been explained by invoking the concept of compatibility (between the water structure and carbohydrate molecules) through a specific hydration model. Galema et al have reported that the relative position of the next-nearest-neighbour hydroxy group within the carbohydrate molecule is the most important one in determining the hydration characteristics, and the extent of hydration is largely determined by the position of OH(4) in conjunction with the relative position of OH(2).

On the basis of compressibility studies Galema and Hoiland have suggested that D-arabinose among the pentoses (D-ribose, D-xylose, and D-lyxose) and D-galactose among the hexoses (D-mannose, and D-glucose) are the least compatible with the water structure. D-fructose (keto-hexose) is less compatible with the water structure than D-glucose. Disaccharides consisting of a glucose and a fructose unit (sucrose, palatinose and turanose), two glucose units (maltose and cellobiose) and glucose and galactose units (melibiose, lactose and lactulose) are the most intermediate and least compatible, respectively with water. Although it is difficult to rationalize completely the $C^{2}_{P^2}$ values in terms of stereochemistry of the saccharide molecules, nevertheless, some important observations can be made: (i) the $C^{2}_{P^2}$ values among the mono-saccharides decrease slightly from the aldopentoses to the aldohexoses to the ketohexoses inspite of an increase in their $C^{2}_{P^2}$ values, which may certainly be ascribed to some stereochemical effects, in the case of D(-)-fructose, the change in the $C^{2}_{P^2}$ value is particularly appreciable; (ii) D(+)-melibiose hemihydrate and D(+)-maltose monohydrate have the largest $C^{2}_{P^2}$ values among the various disaccharides studied.

Among the currently studied disaccharides, the $C^{2}_{P^2}$ values for D(+)-melibiose hemihydrate, D(+)-maltose monohydrate and D(+)-cellobiose decrease in the following order: D(+)-melibiose hemihydrate > D(+)-maltose monohydrate > D(+)-cellobiose.

If it is assumed that the sugars most compatible with the water structure have the least ability to interact with the cosolute molecules and vice versa, then in the light of the compressibility data, the strength of the interactions of the above three saccharides
with the cosolute molecules should decrease in the following order: D(+)-melibiose hemihydrate > D(+)-cellobiose = D(+)-maltose monohydrate.

The higher \( C_{2 \alpha}^0 \) values observed here for D(+)-melibiose hemihydrate fit well in the above order which indicates that this sugar interacts extensively with urea than D(+)-cellobiose and D(+)-maltose monohydrate. However, the appreciable difference between the \( C_{2 \alpha}^0 \) values for D(+)-maltose monohydrate and D(+)-cellobiose is certainly due to a difference in the strength of the interactions with urea, which contradicts the observation made by Galema and Hoiland(1) on the basis of the compressibility data which indicate that maltose and cellobiose have the same hydration characteristics. In addition, Neal and Goring(79) have reported that folding of maltose is more important than in cellobiose due to hydrophobic interactions. If the observation made by Neal and Goring(79) is correct, then the higher \( C_{2 \alpha}^0 \) value for maltose is justified. Because for maltose folding is more important than in cellobiose, its interactions with urea will be stronger than those with cellobiose resulting in a higher \( C_{2 \alpha}^0 \) value. Higher pair interaction coefficients (table 4) for maltose than for cellobiose also support this view. Furthermore, this may also be due to the more flexible \( \alpha_1 \rightarrow 4 \) linkage present in maltose than the \( \beta_1 \rightarrow 4 \) linkage present in cellobiose.83 Similarly, in other disaccharides, folding may occur to different extents as no systematic trend has been observed. As a carbohydrate exists as an equilibrium mixture of several forms in aqueous solutions this complicates the study of stereochemical aspects of hydration in aqueous solutions. Moreover, the presence of urea may influence the position of one or several of these equilibria resulting in even more complexity. Further studies are required to rationalize the stereochemical effects.

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