J Solution Chem (2007) 36:61–80
DOI 10.1007/s10953-006-9100-7

ORIGINAL PAPER

Partial Molar Volumes and Refractions of Aqueous Solutions of Fructose, Glucose, Mannose, and Sucrose at 15.00, 20.00, and 25.00 °C

A. F. Fucaloro · Y. Pu · K. Cha · A. Williams · K. Conrad

Received: 15 April 2006 / Accepted: 6 July 2006 /
Published online: 20 December 2006
© Springer Science+Business Media, LLC 2006

Abstract The partial molar volumes and refractions of aqueous solutions of fructose, glucose, mannose and sucrose were determined at 15.00, 20.00 and 25.00 °C over a wide concentration range. A model is proposed to describe the deviations of the partial molar volumes at higher concentrations from those at infinite dilution. In addition, the partial molar volumes of the sugars at infinite dilution were fit to quadratic relations in temperature.

Keywords Sugars · Monosaccharides · Disaccharides · Molar volume · Partial molar volume · Molar refraction

1 Introduction

Recently, Banipal *et al.* [1] measured the densities of very dilute aqueous solutions of monosaccharides and disaccharides in order to determine the partial molar volumes of sugars at infinite dilution (V_2°). They made separate determinations at 25, 35 and 45 °C in order to investigate the effect of temperature on V_2°. They compared their results to those of previous studies [2–18] and found agreement to within 1% for V_2° determined at 25 °C, with one exception [4]. Therefore, it seems reasonable to assume the reliability of Banipal's results at all temperatures studied. In this study, the measurements for fructose, glucose, mannose and sucrose were extended to higher concentrations in order to determine the effects of concentration on the solute partial molar volume (V_2), in part to determine the approximate sugar concentrations at which their partial molar volumes deviate significantly from the values at infinite dilution (V_2°). The partial molar volumes of both the solute and solvent differ from their values at infinite dilution, and it is worth seeking an interpretation for this deviation. To that end, a model is proposed herein that may be tested, to some extent, with the current results.

A. F. Fucaloro (✉) Y. Pu · K. Cha · A. Williams · K. Conrad
Joint Science Department, Claremont McKenna, Pitzer, and Scripps Colleges, 925 N. Mills Ave., Claremont, CA
e-mail: afucaloro@jsd.claremont.edu

The current study also extends the measurements to lower temperatures in order to get more reliable information about the temperature derivative of V_2°. The conclusion drawn from previous studies [1, 3, 4, 6, 11, 13, 14, 18], including that of Banipal *et al.*, is that the temperature derivative is approximately constant over the temperature range measured from 25 °C and above. However, agreement among the studies is, at best, only fair. Since there is no theoretical requirement that the slope be constant, extending the temperature range to temperatures below 25 °C may reveal deviations from linearity.

2 Methods

2.1 Materials

All sugars were obtained from Sigma Chemicals: D(+) fructose (>99%), D(+)glucose (>99.5%), D(+) mannose (>99%), and sucrose (>99.5%). The sugars were dried before the preparation of the solutions. Varying amounts of sugar (as low as about 20 mg) were added to about 45 g of deionized water to make the solutions.

2.2 Measurements

Densities and refractive indices were measured with an Anton Paar DMA 4500 density meter mated to an Anton Paar 170 refractometer, at temperatures controlled to 0.03 °C with separate Peltier temperature controllers. The uncertainties for the density and refractive index measurements are 0.00002 $\text{g}\cdot\text{mL}^{-1}$ and 0.00005, respectively. Details of the instrumentation and procedure have been given elsewhere [19].

2.3 Molar volume computations

Semi-empirical calculations of each sugar were used to optimize molecular geometries, after which van der Waals volumes were superimposed onto each atom in order to estimate the intrinsic volume of the molecule (V_2^{int}). This procedure is outlined elsewhere [19].

2.4 Data analysis

2.4.1 Molar volume

The molar volume for a binary mixture is a function of the solution density and concentration [19]. Thus,

$$V_m = \frac{x_1 M_1 + x_2 M_2}{\rho} \tag{1}$$

where x_1 and x_2 are the mole fractions of the solvent and solute, respectively, M_1 and M_2 are their molar masses, and ρ is the solution density.

Because the total volume (V) is a homogeneous function of the number of moles of solvent (n_1) and solute (n_2) of rank one, following Euler one may write [20]

$$V = n_1 V_1 + n_2 V_2 \tag{2}$$

where

$$V_1 = \left(\frac{\partial V}{\partial n_1}\right)_{n_2,T,p} \quad \text{and} \quad V_2 = \left(\frac{\partial V}{\partial n_2}\right)_{n_1,T,p}$$

and V_1 and V_2 are the partial molar volumes of solvent and solute, respectively. Dividing both sides of Eq. (2) by n $(= n_1 + n_2)$ yields

$$V_m = x_1 V_1 + x_2 V_2 \tag{3}$$

Fucaloro *et al.* [19] developed a new function, V^*, defined as

$$V^* = \frac{V_m}{x_1} = V_1 + rV_2 \tag{4}$$

where

$$r = \frac{x_2}{x_1} = \frac{n_2}{n_1}$$

By fitting V^* to a polynomial in r, one may determine the partial molar volumes of the solvent and solute as a function of composition. In this manner, the partial molar volumes at infinite dilution for the solvent ($V_1^\bullet$) and solute (V_2°) can be reliably estimated.

A new function analogous to a conventional excess function is defined as

$$V_{\text{ex}}^* = V^* - V_{\text{id}}^* \tag{5}$$

where

$$V_{\text{id}}^* = V_1^\bullet + rV_2^\circ$$

Further, the excess partial molar volumes are defined as

$$V_1^{\text{ex}} = V_1 - V_1^\bullet$$

and

$$V_2^{\text{ex}} = V_2 - V_2^\circ \tag{6}$$

These excess functions provide a measure of the extent to which the solution deviates from ideality as a function of composition.

2.4.2 Molar refraction

The molar refraction is defined as [19, 21, 22]:

$$R_m = f V_m \tag{7}$$

where

$$f = \frac{\left(n_{\mathrm{D}}^2 - 1\right)}{\left(n_{\mathrm{D}}^2 + 2\right)}$$

and n_{D} is the solution refractive index measured using the Na-D spectral doublet. Expressions analogous to those given above for the volume may be written as

$$\begin{aligned} R^* &= R_1 + r R_2 \\ R_{\mathrm{ex}}^* &= R^* - R_{\mathrm{id}}^* \end{aligned}\,. \tag{8}$$

3 Results

Table 1 presents the measured values of ρ and n_{D} and the calculated values of V^* and R^* as functions of r for all of the studied solutions. Figures 1 and 2 show V^* and R^* as a function of r for aqueous fructose solutions at 25 °C. These curves are typical for all systems studied. Figure 3 shows V_{ex}^* as a function of r for fructose at 15, 20 and 25 °C. Similar results were obtained for glucose, mannose and sucrose. Figure 4 shows R_{ex}^* as a function of r for fructose at 25 °C. Similar results were obtained for glucose, mannose and sucrose at all temperatures.

Analysis of the variances (ANOVA) for the polynomial regressions of V^* *versus* r reveals that cubic regressions of the data for aqueous solutions of glucose yield reliable values for all coefficients at all temperatures (the absolute values of the t-test >1.96) whereas quadratic regressions for all other sugar solutions yield reliable values for the coefficients. Table 2 gives the coefficients for the cubic regressions for V^* and V_{ex}^* *versus* r for aqueous glucose and for the quadratic regressions for all of the other aqueous solutions. The subscript "ex" indicates that the coefficients are for the excess function. The coefficients a and b are equivalent to $V_1^\bullet$ and V_2°, respectively. The values of V_2° determined this way agree with those determined by extrapolating the apparent molar volumes to zero concentration by an average difference of 0.1%, with no difference exceeding 0.2%. From Eq. (5), it can be shown that the following relations must hold if the estimates of $V_1^\bullet$ and V_2° are accurate and if a cubic regression gives a reliable representation of the data:

$$\begin{aligned} a_{\mathrm{ex}} &= b_{\mathrm{ex}} = 0 \\ c_{\mathrm{ex}} &= c \\ d_{\mathrm{ex}} &= d \end{aligned}$$

For the quadratic relations there are no d-terms. These relations are seen to hold reasonably well. Also given in Table 2 are the coefficients for the quadratic regression for R^* *versus* r. A quadratic regression yielded reliable values for the coefficients. It is recognized that the molar refraction is more nearly linear with respect to concentration than the molar volume [22]. The coefficients a_R and b_R are equivalent to $R_1^\bullet$ and R_2°, respectively.

Table 1 Values of ρ, n_D, V^* and R^* as functions of composition and temperature

	15 °C				20 °C				25 °C			
r	ρ (g·mL^{-1})	n_D	V^* (mL·mol^{-1})	R^* (mL·mol^{-1})	ρ (g·mL^{-1})	n_D	V^* (mL·mol^{-1})	R^* (mL·mol^{-1})	ρ (g·mL^{-1})	n_D	V^* (mL·mol^{-1})	R^* (mL·mol^{-1})
Fructose												
0	0.99910	1.33341	18.031	3.7131	0.99820	1.33299	18.047	3.7122	0.99705	1.33250	18.068	3.7115
0.000047	0.99929	1.33347	18.036	3.7147	0.99838	1.33305	18.053	3.7139	0.99721	1.33257	18.074	3.7134
0.000106	0.99951	1.33355	18.043	3.7169	0.99861	1.33314	18.059	3.7161	0.99743	1.33265	18.081	3.7156
0.0002190	0.99997	1.33372	18.055	3.7211	0.99905	1.33329	18.072	3.7202	0.99787	1.33281	18.093	3.7197
0.0004290	1.00080	1.33403	18.078	3.7290	0.99988	1.33359	18.094	3.7279	0.99870	1.33310	18.116	3.7274
0.0006394	1.00160	1.33431	18.101	3.7366	1.00068	1.33389	18.118	3.7358	0.99949	1.33340	18.139	3.7353
0.0008447	1.00241	1.33461	18.123	3.7443	1.00148	1.33418	18.140	3.7434	1.00028	1.33368	18.162	3.7428
0.001060	1.00325	1.33491	18.147	3.7522	1.00231	1.33447	18.164	3.7512	1.00100	1.33398	18.188	3.7511
0.001270	1.00406	1.33520	18.170	3.7599	1.00310	1.33476	18.187	3.7590	1.00189	1.33427	18.209	3.7585
0.001503	1.00496	1.33553	18.196	3.7685	1.00399	1.33509	18.213	3.7677	1.00278	1.33460	18.235	3.7672
0.001707	1.00572	1.33581	18.218	3.7761	1.00474	1.33535	18.236	3.7751	1.00352	1.33487	18.258	3.7748
0.001909	1.00652	1.33609	18.240	3.7834	1.00554	1.33564	18.258	3.7825	1.00431	1.33515	18.280	3.7822
0.0021205	1.00733	1.33638	18.263	3.7912	1.00634	1.33593	18.281	3.7903	1.00511	1.33544	18.304	3.7900
0.0031639	1.01125	1.33779	18.378	3.8296	1.01019	1.33729	18.398	3.8285	1.00894	1.33685	18.420	3.8287
0.0042539	1.01540	1.33930	18.497	3.8699	1.01431	1.33879	18.516	3.8687	1.01301	1.33831	18.540	3.8687
0.0053211	1.01931	1.34069	18.614	3.9089	1.01820	1.34019	18.635	3.9080	1.01685	1.33968	18.659	3.9079
0.0063106	1.02294	1.34200	18.722	3.9453	1.02179	1.34152	18.743	3.9447	1.02044	1.34101	18.768	3.9446
0.0085210	1.03085	1.34490	18.965	4.0271	1.02955	1.34435	18.989	4.0263	1.02820	1.34383	19.014	4.0261
0.010596	1.03802	1.34742	19.194	4.1026	1.03673	1.34691	19.218	4.1023	1.03523	1.34639	19.246	4.1026
0.012632	1.04480	1.34953	19.421	4.1737	1.04333	1.34908	19.448	4.1748	1.04184	1.34859	19.476	4.1755
0.012641	1.04498	1.34994	19.419	4.1778	1.04361	1.34944	19.444	4.1779	1.04201	1.34887	19.474	4.1781
0.013583	1.04811	1.35113	19.523	4.2130	1.04665	1.35055	19.550	4.2126	1.04502	1.34993	19.581	4.2124
0.017004	1.05912	1.35507	19.902	4.3382	1.05754	1.35446	19.932	4.3379	1.05588	1.35387	19.963	4.3382
0.019378	1.06657	1.35783	20.164	4.4260	1.06493	1.35716	20.195	4.4254	1.06317	1.35655	20.228	4.4259
0.022323	1.07544	1.36109	20.491	4.5346	1.07372	1.36037	20.524	4.5337	1.07182	1.35969	20.560	4.5341
0.023743	1.07959	1.36236	20.649	4.5840	1.07793	1.36201	20.681	4.5871	1.07609	1.36123	20.716	4.5861
0.024448	1.08172	1.36339	20.726	4.6128	1.07991	1.36268	20.761	4.6124	1.07802	1.36199	20.797	4.6126
0.027380	1.09000	1.36643	21.053	4.7207	1.08818	1.36571	21.088	4.7203	1.08623	1.36501	21.126	4.7207
0.030471	1.09814	1.36946	21.404	4.8350	1.09619	1.36864	21.442	4.8340	1.09415	1.36781	21.482	4.8332
0.033772	1.10724	1.37273	21.765	4.9555	1.10525	1.37206	21.804	4.9564	1.10311	1.37120	21.847	4.9558

Table 1 Continued

	15 °C				20 °C				25 °C			
r	ρ (g·mL^{-1})	n_D	V^* (mL·mol^{-1})	R^* (mL·mol^{-1})	ρ (g·mL^{-1})	n_D	V^* (mL·mol^{-1})	R^* (mL·mol^{-1})	ρ (g·mL^{-1})	n_D	V^* (mL·mol^{-1})	R^* (mL·mol^{-1})
0.034125	1.10874	1.37315	21.793	4.9668	1.10672	1.37239	21.833	4.9668	1.10459	1.37166	21.875	4.9677
0.040691	1.12456	1.37894	22.538	5.2077	1.12234	1.37817	22.583	5.2086	1.12017	1.37756	22.627	5.2112
0.044320	1.13295	1.38195	22.949	5.3400	1.13065	1.38099	22.995	5.3389	1.12869	1.38072	23.035	5.3448
0.051169	1.14870	1.38793	23.708	5.5935	1.14599	1.38675	23.764	5.5916	1.14373	1.38589	23.811	5.5915
0.054213	1.15464	1.39005	24.061	5.7043	1.15230	1.38910	24.110	5.7036	1.14989	1.38836	24.161	5.7059
0.060816	1.16814	1.39509	24.801	5.9471	1.16542	1.39402	24.859	5.9467	1.16307	1.39321	24.910	5.9479
Glucose												
0	0.99910	1.33341	18.031	3.7131	0.99820	1.33299	18.047	3.7122	0.99705	1.33250	18.068	3.7115
0.0000449	0.99927	1.33347	18.036	3.7147	0.99836	1.33306	18.053	3.7140	0.99717	1.33256	18.074	3.7133
0.000109	0.99952	1.33356	18.043	3.7171	0.99861	1.33315	18.060	3.7163	0.99744	1.33265	18.081	3.7156
0.0002151	0.99994	1.33372	18.055	3.7211	0.99903	1.33330	18.071	3.7202	0.99785	1.33281	18.093	3.7196
0.0004253	1.00073	1.33401	18.078	3.7289	0.99982	1.33359	18.095	3.7280	0.99864	1.33309	18.116	3.7273
0.0006490	1.00159	1.33434	18.103	3.7373	1.00067	1.33390	18.120	3.7363	0.99949	1.33342	18.141	3.7358
0.0008631	1.00241	1.33465	18.127	3.7454	1.00148	1.33421	18.144	3.7444	1.00030	1.33372	18.165	3.7438
0.001067	1.00318	1.33494	18.150	3.7530	1.00225	1.33449	18.166	3.7519	1.00105	1.33400	18.188	3.7514
0.001278	1.00398	1.33524	18.173	3.7609	1.00304	1.33478	18.190	3.7597	1.00184	1.33430	18.212	3.7593
0.001500	1.00482	1.33555	18.198	3.7692	1.00388	1.33509	18.215	3.7680	1.00267	1.33461	18.237	3.7676
0.001697	1.00556	1.33585	18.219	3.7768	1.00462	1.33536	18.237	3.7753	1.00340	1.33487	18.259	3.7749
0.001919	1.00639	1.33615	18.244	3.7849	1.00544	1.33566	18.261	3.7835	1.00422	1.33519	18.284	3.7833
0.0021374	1.00721	1.33645	18.268	3.7930	1.00625	1.33596	18.286	3.7916	1.00502	1.33549	18.308	3.7914
0.0032124	1.01118	1.33792	18.388	3.8330	1.01020	1.33740	18.406	3.8314	1.00894	1.33693	18.429	3.8313
0.0044292	1.01563	1.33956	18.523	3.8782	1.01463	1.33904	18.542	3.8766	1.01333	1.33857	18.565	3.8767
0.0053277	1.01887	1.34077	18.623	3.9117	1.01789	1.34024	18.641	3.9099	1.01654	1.33983	18.666	3.9109
0.0064350	1.02280	1.34224	18.747	3.9530	1.02181	1.34169	18.765	3.9511	1.02043	1.34122	18.790	3.9515
0.0085708	1.03022	1.34496	18.985	4.0320	1.02918	1.34440	19.005	4.0302	1.02773	1.34394	19.031	4.0310
0.010742	1.03760	1.34773	19.227	4.1130	1.03655	1.34717	19.247	4.1112	1.03503	1.34672	19.275	4.1124
0.012797	1.04437	1.35026	19.457	4.1895	1.04326	1.34965	19.478	4.1874	1.04169	1.34918	19.507	4.1886
0.013331	1.04616	1.35100	19.516	4.2101	1.04492	1.35034	19.539	4.2080	1.04339	1.34993	19.568	4.2097
0.015071	1.05166	1.35300	19.712	4.2742	1.05050	1.35234	19.734	4.2717	1.04887	1.35188	19.764	4.2733
0.016705	1.05682	1.35489	19.894	4.3345	1.05548	1.35422	19.919	4.3327	1.05393	1.35381	19.949	4.3345
0.018984	1.06389	1.35762	20.148	4.4202	1.06243	1.35684	20.176	4.4176	1.06089	1.35649	20.205	4.4201

Table 1 Continued

	15 °C				20 °C				25 °C			
r	ρ (g·mL^{-1})	n_D	V^* (mL·mol^{-1})	R^* (mL·mol^{-1})	ρ (g·mL^{-1})	n_D	V^* (mL·mol^{-1})	R^* (mL·mol^{-1})	ρ (g·mL^{-1})	n_D	V^* (mL·mol^{-1})	R^* (mL·mol^{-1})
0.021948	1.07240	1.36075	20.486	4.5297	1.07100	1.36004	20.513	4.5276	1.06930	1.35964	20.545	4.5302
0.026573	1.08533	1.36539	21.010	4.6990	1.08411	1.36467	21.033	4.6960	1.08227	1.36419	21.069	4.6984
0.029987	1.09478	1.36912	21.390	4.8278	1.09346	1.36852	21.416	4.8266	1.09161	1.36797	21.452	4.8283
0.033301	1.10320	1.37235	21.768	4.9516	1.10152	1.37138	21.801	4.9476	1.09978	1.37095	21.836	4.9503
0.033306	1.10343	1.37250	21.764	4.9525	1.10200	1.37166	21.793	4.9489	1.09990	1.37111	21.834	4.9518
0.036315	1.11091	1.37522	22.106	5.0630	1.10932	1.37443	22.137	5.0607	1.10748	1.37403	22.174	5.0643
0.039847	1.11914	1.37831	22.512	5.1938	1.11742	1.37763	22.546	5.1935	1.11557	1.37711	22.584	5.1957
0.043509	1.12772	1.38150	22.925	5.3290	1.12589	1.38055	22.963	5.3259	1.12413	1.38020	22.999	5.3298
0.050353	1.14251	1.38699	23.708	5.5814	1.14077	1.38623	23.744	5.5802	1.13879	1.38567	23.785	5.5827
0.053176	1.14852	1.38938	24.027	5.6875	1.14662	1.38838	24.066	5.6839	1.14468	1.38794	24.107	5.6878
0.060372	1.16318	1.39523	24.838	5.9579	1.16078	1.39388	24.890	5.9521	1.15888	1.39364	24.931	5.9587
Mannose												
0	0.99911	1.33341	18.031	3.7130	0.99820	1.33299	18.047	3.7122	0.99705	1.33250	18.068	3.7115
0.0000435	0.99927	1.33347	18.036	3.7147	0.99837	1.33311	18.052	3.7144	0.99721	1.33256	18.073	3.7131
0.000107	0.99953	1.33357	18.043	3.7171	0.99862	1.33315	18.059	3.7162	0.99746	1.33266	18.080	3.7156
0.000232	1.00000	1.33374	18.057	3.7217	0.99908	1.33332	18.073	3.7209	0.99792	1.33283	18.095	3.7202
0.000433	1.00078	1.33403	18.079	3.7292	0.99986	1.33360	18.096	3.7283	0.99869	1.33311	18.117	3.7276
0.00065	1.00160	1.33434	18.103	3.7373	1.00068	1.33391	18.120	3.7364	0.99950	1.33342	18.141	3.7358
0.000847	1.00236	1.33461	18.125	3.7446	1.00143	1.33419	18.142	3.7438	1.00025	1.33369	18.163	3.7431
0.001077	1.00324	1.33493	18.150	3.7530	1.00230	1.33450	18.167	3.7522	1.00112	1.33401	18.189	3.7516
0.001267	1.00396	1.33520	18.171	3.7602	1.00302	1.33476	18.188	3.7592	1.00183	1.33428	18.210	3.7588
0.001497	1.00484	1.33551	18.197	3.7686	1.00389	1.33509	18.214	3.7678	1.00269	1.33459	18.236	3.7672
0.001696	1.00559	1.33581	18.219	3.7762	1.00464	1.33536	18.236	3.7751	1.00343	1.33486	18.258	3.7746
0.001907	1.00638	1.33610	18.242	3.7840	1.00543	1.33565	18.259	3.7830	1.00422	1.33516	18.281	3.7825
0.0021290	1.00721	1.33640	18.267	3.7922	1.00626	1.33596	18.284	3.7913	1.00505	1.33545	18.306	3.7906
0.0031787	1.01113	1.33782	18.383	3.8309	1.01014	1.33735	18.401	3.8298	1.00891	1.33685	18.424	3.8294
0.0043089	1.01527	1.33933	18.509	3.8727	1.01427	1.33888	18.527	3.8719	1.01301	1.33836	18.550	3.8713
0.0052984	1.01886	1.34064	18.618	3.9093	1.01783	1.34019	18.637	3.9086	1.01654	1.33967	18.661	3.9081
0.0063895	1.02274	1.34208	18.740	3.9498	1.02169	1.34162	18.759	3.9491	1.02037	1.34108	18.784	3.9486
0.0085118	1.03020	1.34481	18.975	4.0283	1.02910	1.34432	18.996	4.0274	1.02771	1.34375	19.021	4.0269
0.012781	1.04459	1.35015	19.450	4.1868	1.04331	1.34958	19.474	4.1858	1.04188	1.34902	19.501	4.1855

Table 1 Continued

	15 °C				20 °C				25 °C			
r	ρ (g·mL^{-1})	n_D	V^* (mL·mol^{-1})	R^* (mL·mol^{-1})	ρ (g·mL^{-1})	n_D	V^* (mL·mol^{-1})	R^* (mL·mol^{-1})	ρ (g·mL^{-1})	n_D	V^* (mL·mol^{-1})	R^* (mL·mol^{-1})
0.013769	1.04778	1.35134	19.561	4.2235	1.04655	1.35080	19.584	4.2226	1.04511	1.35022	19.611	4.2222
0.015578	1.05346	1.35335	19.765	4.2895	1.05227	1.35284	19.787	4.2888	1.05083	1.35221	19.814	4.2878
0.017377	1.05910	1.35540	19.966	4.3557	1.05776	1.35485	19.991	4.3552	1.05635	1.35427	20.018	4.3546
0.019084	1.06433	1.35733	20.156	4.4188	1.06299	1.35680	20.182	4.4185	1.06153	1.35617	20.210	4.4176
0.019708	1.06628	1.35814	20.225	4.4429	1.06489	1.35755	20.252	4.4421	1.06342	1.35698	20.280	4.4419
0.021757	1.07240	1.36028	20.454	4.5173	1.07096	1.35976	20.481	4.5175	1.06941	1.35915	20.511	4.5172
0.022665	1.07497	1.36133	20.557	4.5520	1.07357	1.36076	20.584	4.5515	1.07207	1.36025	20.613	4.5520
0.024346	1.07986	1.36315	20.745	4.6142	1.07840	1.36257	20.773	4.6139	1.07680	1.36192	20.804	4.6133
0.024868	1.08137	1.36367	20.802	4.6330	1.07994	1.36317	20.830	4.6335	1.07828	1.36250	20.862	4.6329
0.025919	1.08436	1.36482	20.920	4.6724	1.08286	1.36424	20.949	4.6722	1.08128	1.36364	20.979	4.6721
0.027476	1.08861	1.36640	21.096	4.7300	1.08714	1.36583	21.124	4.7298	1.08553	1.36526	21.156	4.7302
0.034425	1.10677	1.37297	21.881	4.9846	1.10523	1.37245	21.911	4.9854	1.10358	1.37156	21.944	4.9822
Sucrose												
0	0.99911	1.33341	18.031	3.7130	0.99820	1.33299	18.047	3.7122	0.99704	1.33250	18.068	3.7115
0.0000255	0.99931	1.33349	18.036	3.7149	0.99840	1.33307	18.053	3.7141	0.99724	1.33258	18.074	3.7133
0.0000570	0.99952	1.33357	18.043	3.7172	0.99862	1.33315	18.059	3.7163	0.99745	1.33266	18.081	3.7156
0.0001157	0.99995	1.33373	18.055	3.7213	0.99904	1.33331	18.072	3.7205	0.99787	1.33282	18.093	3.7197
0.0002243	1.00075	1.33403	18.078	3.7290	0.99984	1.33360	18.095	3.7281	0.99867	1.33312	18.116	3.7275
0.0003415	1.00161	1.33434	18.103	3.7373	1.00067	1.33392	18.120	3.7365	0.99951	1.33344	18.141	3.7359
0.0004472	1.00237	1.33463	18.125	3.7448	1.00145	1.33420	18.142	3.7439	1.00027	1.33371	18.163	3.7432
0.000562	1.00322	1.33502	18.149	3.7537	1.00229	1.33450	18.166	3.7519	1.00110	1.33402	18.188	3.7514
0.000674	1.00403	1.33531	18.172	3.7615	1.00309	1.33481	18.190	3.7599	1.00190	1.33432	18.211	3.7593
0.000782	1.00481	1.33559	18.195	3.7691	1.00386	1.33510	18.213	3.7677	1.00267	1.33461	18.234	3.7670
0.000898	1.00565	1.33591	18.220	3.7774	1.00470	1.33540	18.237	3.7758	1.00351	1.33492	18.259	3.7752
0.001038	1.00666	1.33628	18.249	3.7873	1.00571	1.33577	18.266	3.7856	1.00450	1.33528	18.288	3.7851
0.0011279	1.00730	1.33652	18.268	3.7937	1.00635	1.33601	18.285	3.7920	1.00514	1.33552	18.307	3.7915
0.0016754	1.01118	1.33791	18.384	3.8320	1.01022	1.33741	18.401	3.8305	1.00897	1.33693	18.424	3.8302
0.0022344	1.01512	1.33938	18.502	3.8717	1.01411	1.33887	18.520	3.8703	1.01287	1.33837	18.543	3.8698
0.0027901	1.01899	1.34080	18.619	3.9110	1.01796	1.34028	18.638	3.9096	1.01669	1.33978	18.661	3.9092
0.0033544	1.02287	1.34226	18.738	3.9514	1.02180	1.34172	18.758	3.9498	1.02054	1.34123	18.781	3.9495
0.0044838	1.03043	1.34503	18.979	4.0313	1.02935	1.34447	18.999	4.0297	1.02807	1.34402	19.022	4.0298

Table 1 Continued

	15 °C				20 °C				25 °C			
r	ρ (g·mL^{-1})	n_D	V^* (mL·mol^{-1})	R^* (mL·mol^{-1})	ρ (g·mL^{-1})	n_D	V^* (mL·mol^{-1})	R^* (mL·mol^{-1})	ρ (g·mL^{-1})	n_D	V^* (mL·mol^{-1})	R^* (mL·mol^{-1})
0.0055714	1.03758	1.34767	19.210	4.1087	1.03649	1.34723	19.230	4.1083	1.03512	1.34666	19.256	4.1076
0.0065799	1.04406	1.35009	19.426	4.1809	1.04276	1.34913	19.450	4.1757	1.04148	1.34904	19.474	4.1798
0.0066939	1.04477	1.35036	19.450	4.1891	1.04365	1.34981	19.471	4.1876	1.04220	1.34924	19.498	4.1872
0.0071838	1.04795	1.35159	19.553	4.2246	1.04675	1.35096	19.576	4.2226	1.04533	1.35046	19.602	4.2228
0.0079453	1.05272	1.35340	19.716	4.2795	1.05148	1.35270	19.739	4.2769	1.05002	1.35217	19.767	4.2770
0.0089871	1.05902	1.35565	19.941	4.3532	1.05771	1.35497	19.966	4.3511	1.05626	1.35447	19.993	4.3514
0.0095955	1.06263	1.35705	20.073	4.3975	1.06142	1.35628	20.096	4.3940	1.05994	1.35591	20.124	4.3959
0.010116	1.06582	1.35823	20.184	4.4348	1.06454	1.35765	20.208	4.4337	1.06297	1.35703	20.238	4.4332
0.011089	1.07145	1.36031	20.395	4.5046	1.07011	1.35962	20.420	4.5025	1.06857	1.35907	20.450	4.5027
0.011658	1.07476	1.36153	20.517	4.5454	1.07340	1.36084	20.543	4.5434	1.07181	1.36031	20.574	4.5440
0.012256	1.07811	1.36280	20.648	4.5888	1.07677	1.36214	20.674	4.5870	1.07519	1.36161	20.704	4.5876
0.012759	1.08103	1.36394	20.756	4.6257	1.07966	1.36332	20.782	4.6245	1.07802	1.36267	20.814	4.6240
0.013231	1.08361	1.36490	20.859	4.6598	1.08224	1.36422	20.886	4.6579	1.08068	1.36373	20.916	4.6589
0.014094	1.08837	1.36665	21.047	4.7219	1.08692	1.36596	21.075	4.7203	1.08531	1.36540	21.106	4.7207
0.014892	1.09251	1.36820	21.225	4.7798	1.09110	1.36749	21.252	4.7777	1.08952	1.36704	21.283	4.7793
0.017541	1.10635	1.37324	21.806	4.9707	1.10493	1.37259	21.834	4.9694	1.10322	1.37215	21.868	4.9717
0.022862	1.13199	1.38285	22.987	5.3602	1.13029	1.38194	23.022	5.3569	1.12855	1.38154	23.057	5.3601
0.027732	1.15328	1.39091	24.084	5.7209	1.15158	1.39006	24.120	5.7183	1.14972	1.38949	24.159	5.7200

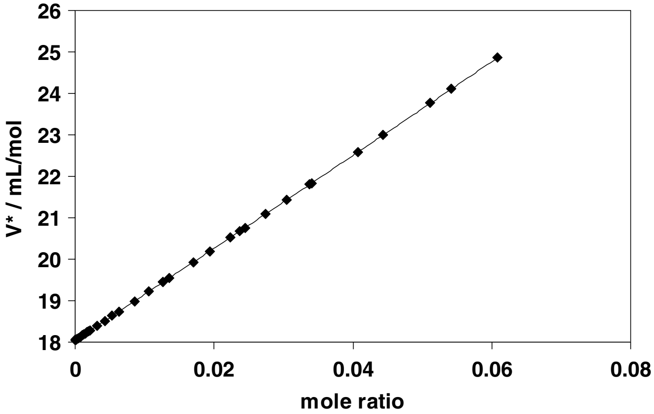

Fig. 1 Plot of V^* *versus* r for fructose at 25 °C

4 Discussion

4.1 A solution model

Around each solute molecule is a region of water molecules for which the properties of the water differ from those of the bulk water. Hereafter, water in this region will be referred to as coordinated water, though it is understood that not all of these water molecules are necessarily hydrogen bonded to the solute molecule. Thus, the molar volume of the bulk water ($V_{1b}^{\bullet}$) and the average molar volume of the coordinated water (V_1^{coord}) are not, in general, equal. Since it is reasonable to assume that there exist concentric shells of coordinated water each with its own properties, V_1^{coord} ought to be understood as an average value. In the subsequent discussion the degree of solute-solute association is considered to be negligible.

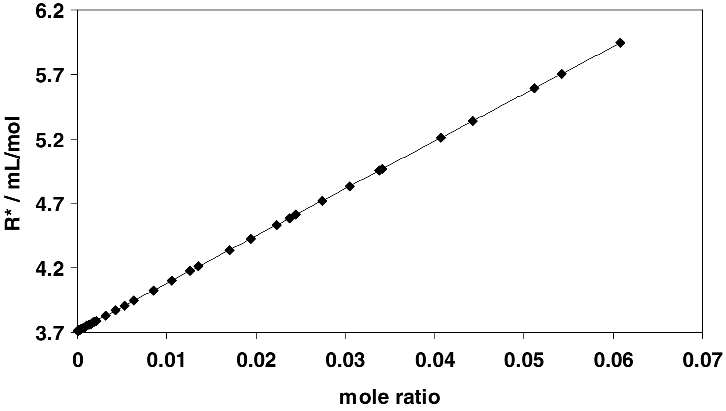

Fig. 2 Plot of R^* *versus* r for fructose at 25 °C

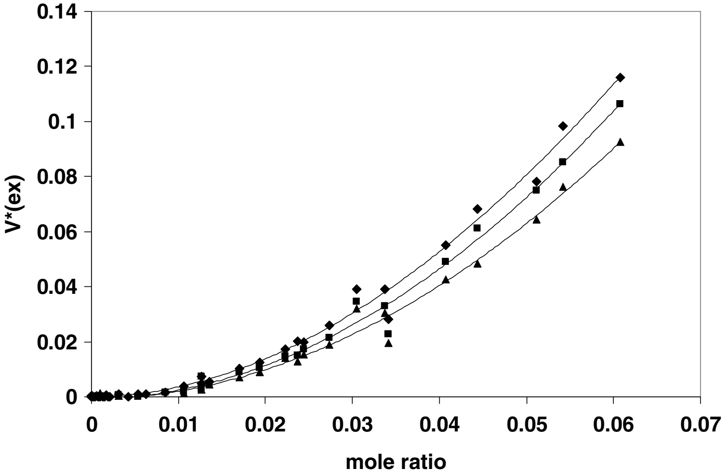

Fig. 3 Plot of V_{ex}^{*} *versus* r for fructose at 15 (diamond), 20 (square), and 25 °C (triangle)

For q coordinated water molecules per solute molecule, the total volume of a solution of n_1 moles of water molecules and n_2 moles of solute molecules is given by

$$V = (n_1 - qn_2)V_{1b}^{\bullet} + n_2 V_{\text{SW}_q} = n_1 V_{1b}^{\bullet} + n_2(V_{\text{SW}_q} - qV_{1b}^{\bullet}) = n_1 V_{1b}^{\bullet} + n_2 Z \tag{9}$$

where V_{SW_q} is the volume of the solute molecule (V_2^{sol}) and its coordinated water molecules. The partial molar volumes are determined from their definitions as follows:

$$V_1 = \left(\frac{\partial V}{\partial n_1}\right)_{n_2,T,p} = V_{1b}^{\bullet} + n_2\left(\frac{\partial Z}{\partial n_1}\right)_{n_2,T,p}$$

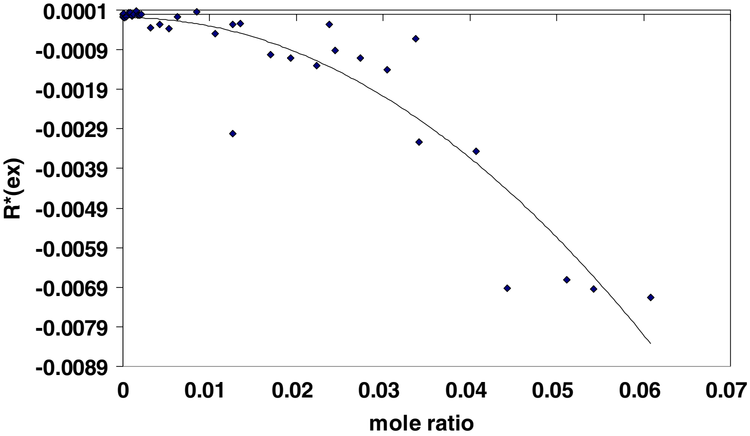

Fig. 4 Plot of R_{ex}^{*} *versus* r for fructose at 25 °C

Table 2 Polynomial coefficients[a] for $V^*(= a + br + cr^2 + dr^3)^b$, $V^*_{\mathrm{ex}}(= a_{\mathrm{ex}} + b_{\mathrm{ex}}r + c_{\mathrm{ex}}r^2 + d_{\mathrm{ex}}r^3)^b$, and $R^*(= a_R + b_Rr + c_Rr^2)$

	a	a_{ex}	b	b_{ex}	$c = c_{\mathrm{ex}}$	$d = d^b_{\mathrm{ex}}$	a_R	b_R	c_R
Fructose									
15 °C	18.031(0.001)	−0.0002	109.54(0.08)	−0.005	29.9(1.6)	–	3.7131(0.0003)	36.78(0.03)	−0.9(0.6)
20 °C	18.047(0.001)	−0.0007	110.29(0.08)	−0.004	28.5(1.5)	–.	3.7121(0.0001)	36.86(0.02)	−2.3(0.5)
25 °C	18.068(0.001)	−0.0007	110.99(0.08)	0.002	24.8(1.4)	–	3.7112(0.0002)	36.90(0.02)	−2.1(0.4)
Glucose									
15 °C	18.031(0.000)	0.0006	110.62(0.13)	−0.660	60.7(5.9)	−407(70)	3.7134(0.0002)	37.20(0.03)	−1.0(0.5)
20 °C	18.048(0.000)	−0.0003	111.18(0.13)	−0.398	50.7(6.0)	−245(71)	3.7122(0.0002)	37.16(0.02)	−1.0(0.5)
25 °C	18.069(0.000)	−0.0002	111.88(0.10)	−0.346	42.5(4.6)	−211(54)	3.7118(0.0003)	37.28(0.03)	−1.7(0.6)
Mannose									
15 °C	18.031(0.000)	0.0000	110.71(0.05)	−0.001	31.4(1.6)	–	3.7131(0.0001)	37.09(0.02)	−3.8(0.8)
20 °C	18.047(0.000)	0.0003	111.27(0.04)	0.004	27.5(1.4)	–	3.7123(0.0001)	37.07(0.02)	−1.9(0.7)
25 °C	18.068(0.000)	0.0004	111.72(0.03)	0.003	24.5(0.9)	–	3.7115(0.0002)	37.16(0.04)	−5.7(1.6)
Sucrose									
15 °C	18.031(0.000)	0.0001	209.88(0.04)	0.004	82.2(1.9)	–	3.7134(0.0001)	70.70(0.03)	−11.8(1.1)
20 °C	18.048(0.000)	0.0005	210.73(0.06)	0.001	76.5(2.4)	–	3.7122(0.0002)	70.60(0.05)	−10.1(2.3)
25 °C	18.068(0.000)	0.0005	211.55(0.03)	−0.005	69.3(1.4)	–	3.7115(0.0001)	70.74(0.02)	−11.3(0.9)

[a] Cubic regressions are used for aqueous glucose and quadratic regressions for the other aqueous solutions. (See the text.)

[b] Deviations are reported in parentheses.

and

$$V_2 = \left(\frac{\partial V}{\partial n_2}\right)_{n_1,T,p} = Z + n_2\left(\frac{\partial Z}{\partial n_2}\right)_{n_1,T,p}$$

Using the definition for the mole ratio, r, it can be shown that

$$\left(\frac{\partial r}{\partial n_1}\right)_{n_2} = -\frac{n_2}{n_1^2}$$

and

$$\left(\frac{\partial r}{\partial n_2}\right)_{n_1} = \frac{1}{n_1}$$

By substitution of these expressions into those for the partial molar volumes, one obtains

$$V_1 = V_{1b}^{\bullet} - r^2\left(\frac{dZ}{dr}\right) \tag{10}$$

and

$$V_2 = Z + r\left(\frac{dZ}{dr}\right) \tag{11}$$

Since $V_{1b}^{\bullet}$ is the molar volume of bulk water and therefore constant, compatibility with the Gibbs-Duhem equation is assured.

It is now assumed that V_{SW_q} is the sum of three terms such that

$$V_{\mathrm{SW}_q} = V_2^{\mathrm{sol}} + qV_1^{\mathrm{coord}} = V_2^{\mathrm{int}} + V_2^{\mathrm{void}} + qV_1^{\mathrm{coord}}, \tag{12}$$

where V_2^{int} is the solute's intrinsic molar volume that may be estimated computationally by superimposing van der Waals radii onto quantum mechanically optimized structures, and V_2^{void} is the void volume arising from imperfect packing of the solute molecules in solution [19, 23]. For dilute solutions, it is reasonable to assume that these terms are nearly constant with respect to concentration. The qV_1^{coord} term is the total volume of coordinated water per solute molecule. It is this term that is expected to vary with concentration, even for fairly dilute solutions. As the concentration of the solute increases, there is an increased probability of interactions between neighboring coordinated water regions that would result in a reduced value for q due to overlap of these regions and a change in V_1^{coord}, the average molar volume of coordinated water. Substituting Eq. (12) into Eqs. (10) and (11) and taking into account the definition of Z implied in Eq. (9), one obtains

$$V_1 = V_{1b}^{\bullet} + r^2\left(\frac{d\left[q\Delta V_1\right]}{dr}\right) \tag{13}$$

and

$$V_2 = \left(V_2^{\text{sol}} - q\Delta V_1\right) - r\left(\frac{d\,[q\Delta V_1]}{dr}\right), \tag{14}$$

where

$$\Delta V_1 = V_{1b}^{\bullet} - V_1^{\text{coord}}.$$

Substitution of Eqs. (13) and (14) into Eq. (4) yields

$$V^* = V_{1b}^{\bullet} + r\left(V_2^{\text{sol}} - q\Delta V_1\right) \tag{15}$$

where $V_{1b}^{\bullet}$ and V_2^{sol} are assumed to be constant (see above) and the deviation from linearity comes from the $q\Delta V_1$ term. At infinite dilution, q is probably a maximum value (q°) as discussed above. The functionality of ΔV_1 with concentration is not known and the following designations for ΔV_1 and V_1^{coord} are given for their values at infinite dilution: ΔV_1° and $V_1^{\text{coord}[\circ]}$, respectively. Assuming that $(\frac{d[q\Delta V_1]}{dr})$ is zero in the limit of infinite dilution, the partial molar volumes at infinite dilution become

$$V_1^{\bullet} = V_{1b}^{\bullet} \tag{16}$$

and

$$V_2^\circ = V_2^{\text{sol}} - q^\circ\Delta V_1^\circ = V_2^{\text{sol}} - q^\circ(V_{1b}^{\bullet} - V_1^{\text{coord}[\circ]}) \tag{17}$$

Substitution of these equations into Eqs. (5) and (6) gives

$$V_1^{\text{ex}} = r^2\left(\frac{d\,[q\Delta V_1]}{dr}\right) \tag{18}$$

$$V_2^{\text{ex}} = \left(q^\circ\Delta V_1^\circ - q\Delta V_1\right) - r\left(\frac{d[q\Delta V_1]}{dr}\right) \tag{19}$$

and

$$V_{\text{ex}}^* = r\left(q^\circ\Delta V_1^\circ - q\Delta V_1\right) \tag{20}$$

There is a concentration region for which the value of the excess function is nearly zero. This is evident for fructose at all temperatures as shown in Fig. 3. This behavior is typical for all of the studied solutions at all temperatures. Moreover, the same type of behavior is observed for R_{ex}^* (see Fig. 4). In this region, the value for $q\Delta V_1$ is equal, or nearly equal, to its value at infinite dilution (*i.e.*, the quantity $[q^\circ\Delta V_1^\circ - q\Delta V_1]$ approaches zero as r approaches zero). As the concentration increases beyond this "ideal" region, the excess volume function becomes increasingly positive (see Fig. 3), suggesting that the $q\Delta V_1$ term decreases with increasing concentration. It was assumed earlier that q decreases with increasing concentration. If one further assumes that ΔV_1 remains fairly constant with respect to concentration such that $\Delta V_1 \cong \Delta V_1^\circ$, then ΔV_1 must be positive, or more specifically, $V_{1b}^{\bullet} > V_1^{\mathrm{coord}}$. Using this approximation, then Eq. (20) becomes

$$V_{\mathrm{ex}}^* = r(q^\circ - q)\Delta V_1^\circ \tag{21}$$

Expanding q about q° using a Taylor expansion containing three terms yields

$$q = q^\circ + q_1 r + q_2 r^2 \tag{22}$$

where

$$q_1 = \left(\frac{dq}{dr}\right) \quad \text{and} \quad q_2 = \left(\frac{1}{2}\right)\left(\frac{d^2q}{dr^2}\right)$$

The expansion may be truncated after the second term for a quadratic expansions of V^*, as is the case for all the studied sugars with the exception of glucose (see Results). For generality, the ensuing development includes the third term of the expansion. Substitution into Eq. (21) gives

$$V_{\mathrm{ex}}^* = -\Delta V_1^\circ(q_1 r^2 + q_2 r^3) \tag{23}$$

where (see Table 2)

$$c = c_{\mathrm{ex}} = -\Delta V_1^\circ q_1 \text{ and}$$
$$d = d_{\mathrm{ex}} = -\Delta V_1^\circ q_2$$

It is posited above that the c-term is the negative of the product of a positive (ΔV_1°) and a negative ($\frac{dq}{dr}$) term, and therefore is positive. Table 2 confirms this and shows moreover that this term decreases with increasing temperature in all cases. The reason for this behavior with temperature is unclear. One also notes that the d-term for aqueous glucose is negative and becomes decreasingly so with increasing temperature. From this one may infer that $\frac{d^2q}{dr^2}$ is positive.

4.2 Partial molar volumes as a function of temperature

The values for the partial molar volumes at infinite dilution are reported in Table 3 along with those determined in some of the earlier studies, a majority of which were conducted at 25 °C and some of which were reported at 35 and 45 °C . The current results cover 15, 20 and 25 °C. In reviewing earlier studies, some of which are included in Table 3, Banipal *et al.* [1] noted that the V_2° values reported for all sugars at 25 °C agree within 1% with the exception of those reported by Paljk *et al.* [4]. The current results at 25 °C also fall within this 1% range. Moreover, these results fall within 0.2% of those of Banipal *et al.* [1] for all four sugars and within 0.1% excluding sucrose. This suggested that it might be useful to compare our results with those of Banipal *et al.* over the temperature range of 15 to 45 °C. Figure 5 shows V_2° as a function of temperature for the sugars studied here and those studied by Banipal. The current results are reported for 15 and 20 °C, Banipal's results for 35 and 45 °C, and the average of our results and Banipal's at 25 °C. The values for sucrose have been multiplied by the ratio of the molar mass of the monosaccharide to that of sucrose (a

Table 3 Values of V_2° (mL·mol^{-1})^a as a function of temperature

	15 °C	20 °C	25 °C	35 °C	45 °C	Ref.
Fructose	109.54(0.08)	110.29(0.08)	110.99(0.08)			This work
			111.06	112.12	112.96	1
			113.4	114.5	115.5	4
			110.4			9
Glucose	110.62(0.13)	111.18(0.13)	111.88(0.10)			This work
			111.91	112.82	113.59	1
			111.79			8
			112.7	113.5	114.2	4
			112.2			9
			111.5			15
Mannose	110.71(0.05)	111.27(0.04)	111.72(0.03)			This work
			111.70	112.30	112.96	1
			112.6	113.4	114.1	4
			111.7			9
Sucrose	209.88(0.04)	210.73(0.06)	211.55(0.03)			This work
			211.92	212.74	213.81	1
			211.39			8
			210.2			9
			211			15

^{a}Deviations are reported in parentheses.

disaccharide) for purposes of easy comparison on the graph. The lines are quadratic fits in temperature for each sugar. The coefficients for the quadratic fits are listed in Table 4. The values of $(\frac{\partial V_2^\circ}{\partial T})_p$ as a function of temperature may be calculated from these coefficients. In all cases, the derivatives decrease with increasing temperature.

Banipal *et al.* [1] concluded that V_2° is a linear function of temperature based upon measurements of V_2° at three temperatures. Using results over an expanded temperature range suggests a more complicated relationship between V_2° and T, perhaps a quadratic relationship (see Table 4). Analytical expressions for $(\frac{\partial V_2^\circ}{\partial T})_p$ can be determined as a function of temperature and these values are reported in Fig. 6.

4.3 Partial molar volumes at infinite dilution

The partial molar volume of solute at infinite dilution has been described as the addition of the intrinsic volume of the solute, a contribution from solute-solvent interactions (V_2^{void}) [19, 23], and a term reflecting the difference in molar volumes of the bulk and coordinated water. The variation of V_2° with temperature is almost certainly the result of changes in the last two terms. Attempts to separate the contributions by comparing V_2° to the molar volume of the solute solid may be problematic since molecular packing in crystals depends on many factors, not least of which is the molecular shape. It might be instructive to compare V_2° to the intrinsic molar volume (V_2^{int}) computed by molecular modeling, which optimizes molecular geometry prior to calculating a molar volume using the standard van der Waals radii (see Methods, 2.3).

Banipal *et al.* [1] report the partial molar volumes at infinite dilution (V_2°) and the molar volumes of solids (V_2^{solid}) for a series of sugars at 25 °C, with the exception of sucrose for which the crystal density was measured at 15 °C. They found that the difference between

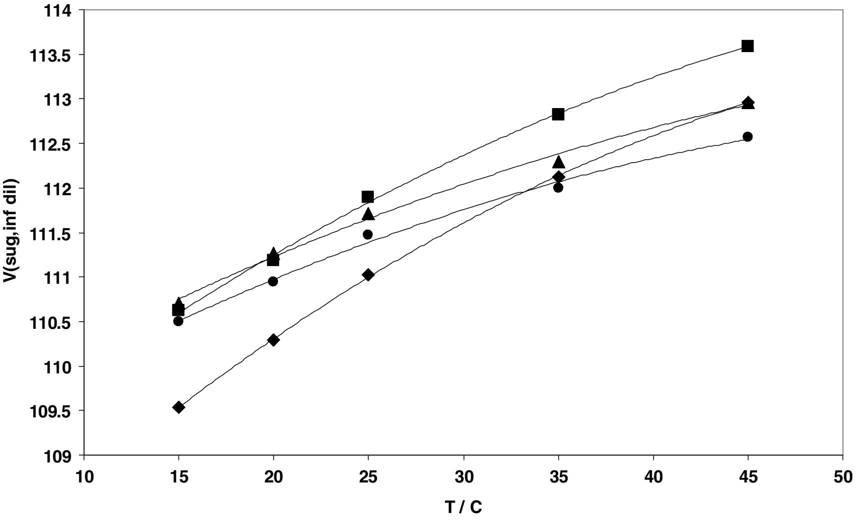

Fig. 5 Plot of V_2° *versus* temperature for fructose (*diamond*), glucose (*square*), mannose (*triangle*), and sucrose (*circle*). The actual values for sucrose have been multiplied by the ratio of the molar masses of monosaccharide to the disaccharide for ready comparison with the monosaccharides (see the text)

these values,

$$\Delta V_2^{\text{solid}} = V_2^\circ - V_2^{\text{solid}} \tag{24}$$

is almost always negative and is negative for the sugars studied here (see Table 5). Bernal and van Hook [17] concluded the same behavior is true for carbohydrates in general. It is assumed here that V_2^{solid} can be considered to be the sum of the intrinsic volume discussed earlier and the void volume accounting for the molecular packing in the crystal. Thus,

$$V_2^{\text{solid}} = V_2^{\text{int}} + V_{2\text{solid}}^{\text{void}} \tag{25}$$

Substituting Eq. (17) into Eqs. (24) and (25) and assuming that V_2^{sol} is the sum of V_2^{int} and V_2^{void} (see above), one obtains

$$\Delta V_2^{\text{solid}} = \left(V_2^{\text{void}} - V_{2\text{solid}}^{\text{void}}\right) - q^\circ\left(V_{1b}^{\bullet} - V_1^{\text{coord}[\circ]}\right) \tag{26}$$

Table 4 Values of the parameters for $V_2^\circ = a + bT + cT^2$ where the temperature is in °C

	a^a	b^a	c^a
Fructose	106.75(0.01)	0.210(0.001)	–0.00160(0.00002)
Glucose	108.228(0.24)	0.173(0.018)	–0.00122(0.00030)
Mannose	109.07(0.35)	0.125(0.026)	–0.00088(0.00042)
Sucrose^b	108.80(0.33)	0.129(0.024)	–0.00102(00040)

[a] Deviations are reported in parentheses.
[b] Using the adjusted molar mass (see text).

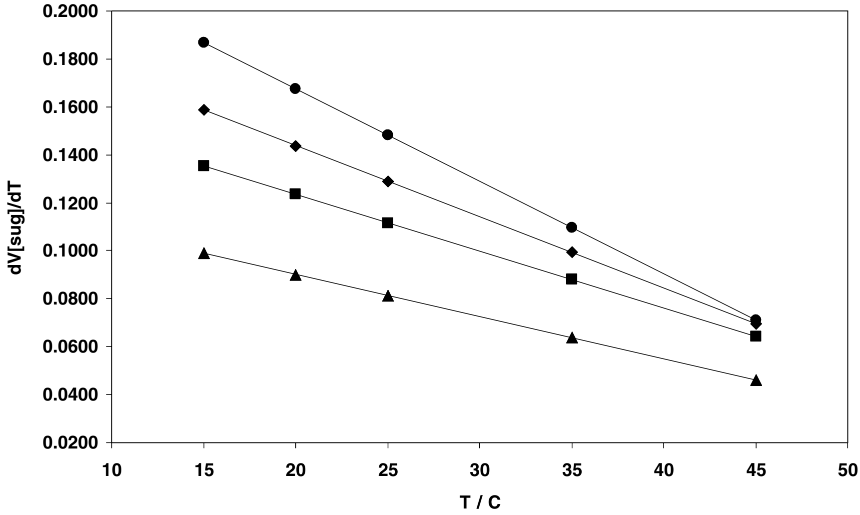

Fig. 6 Plot of $(\frac{\partial V_2^\circ}{\partial T})_p$ *versus* temperature for fructose (*diamond*), glucose (*square*), mannose (*triangle*), and sucrose (*circle*)

The sign of the first term is not known, but $(V_{1b}^{\bullet} - V_1^{\mathrm{coord}})$ is positive as discussed earlier.

Also reported in Table 5 is the difference between the partial molar volumes at infinite dilution at 25 °C and the intrinsic volumes for each sugar studied here. Thus,

$$\Delta V_2^{\mathrm{int}} = V_2^\circ - V_2^{\mathrm{int}}$$

and

$$\Delta V_2^{\mathrm{int}} = V_2^{\mathrm{void}} - q^\circ\left(V_{1b}^{\bullet} - V_1^{\mathrm{coord}[\circ]}\right) \tag{27}$$

All values of $\Delta V_2^{\mathrm{int}}$ for the monosaccharides are about the same and are roughly half that for sucrose. Since the second term is negative, it can be assumed that the void volumes are appreciably large.

Subtracting V_2^{int} from V_2^{solid} provides estimates of $V_{2\mathrm{solid}}^{\mathrm{void}}$ (see Eq. (25)) and these values for the sugars studied here are also reported in Table 5. It is noteworthy that $V_{2\mathrm{solid}}^{\mathrm{void}}$ accounts for 14.6 to 17.3% of the molar volume of the solid. Although it is not possible to estimate the void volumes in a solution, one can set a lower limit using Eq. (27).

Table 5 Various volumes defined in the text (units mL·mol^{-1})

	V_2° at 25 °C	V_2^{int}	V_2^{solid}	$\Delta V_2^{\mathrm{int}}$	$\Delta V_2^{\mathrm{solid}}$	$V_{2\mathrm{solid}}^{\mathrm{void}}$
Fructose	111.01	96.21	112.60	14.80	–1.59	16.39
Glucose	111.90	95.74	115.34	16.16	–3.44	19.60
Mannose	111.75	95.63	115.19	16.12	–3.44	19.56
Sucrose	211.74	178.23	215.49	33.51	–3.76	37.27

Table 6 Values of R_2° (mL·mol^{-1})^a as a function of temperature

	15 °C	20 °C	25 °C	Computed
Fructose	36.78(0.03)	36.86(0.02)	36.90(0.02)	37.150
Glucose	37.20(0.03)	37.16(0.02)	37.28(0.03)	37.150
Mannose	37.09(0.02)	37.07(0.02)	37.16(0.04)	37.150
Sucrose	70.70(0.03)	70.60(0.05)	70.74(0.02)	70.837

[a] Deviations are reported in parentheses.

4.4 Partial molar refractions

Table 6 reports the partial molar refractions at infinite dilution (R_2°) at 15, 20 and 25 °C. Also included are the molar refractions of the sugars computed using the tabulated data developed by Vogel [24]. The computed values are the same for the three isomeric monosaccharides. The measured values are not particularly sensitive to temperature and are fairly close to the computed values. Fructose, among the monosaccharides, exhibits the greatest difference between the computed and measured values. Perhaps this occurs because, as the only monosaccharide with a five-membered ring, it exhibits the greatest steric strain that, in turn, affects its electronic structure.

The molar refraction as a function of concentration exhibits a domain for which the partial molar refractions of water and each sugar are constant and equal to the values at infinite dilution. (See Fig. 4; all of the studied sugars at all temperatures exhibit similar behavior.) This ideal domain extends to about $r = 0.001$, which is consistent with the conclusion drawn from the molar volume data. Beyond the ideal domain, the molar refractions of the sugars decrease while that of water increases. The reason for this behavior is unclear.

Acknowledgment This work was supported by a grant from Claremont McKenna College awarded to A.F. by President Pamela Gann.

References

1. Banipal, P.K., Banipal, T.S., Lark, B.S. Ahluwalia, J.C.: Partial molar heat capacities and volumes of some mono-, di- and tri-saccharides in water at 298.15, 308.15 and 318.15 K. J. Chem. Soc., Faraday Trans. **93**, 81–87 (1997)
2. Jasra, R.V., Ahluwalia, J C.: Enthalpies and heat-capacities of dissolution, apparent molar heat-capacities, and apparent molar volumes of some mono-saccharides, di-saccharides, tri-saccharides, and tetra-saccharides in water. J. Chem. Thermodyn **16**, 583–590 (1984)
3. Goldberg, R.N., Tewari, Y.B.: Thermodynamic and transport-properties of carbohydrates and their monophosphates – the pentoses and hexoses. J. Phys. Chem. Ref. Data, Suppl. **18**, 809–880 (1989)
4. Paljk, S., Klofutar, C., Kac, M.: Partial molar volumes and expansibilities of some D-pentoses and D-hexoses in aqueous solution. J. Chem. Eng. Data **35**, 41–43 (1990)
5. Hoiland, H., Holvik, H.: Partial molar volumes and compressibilities of carbohydrates in water J. Solution Chem. **7**, 587–596 (1978)
6. Franks, F., Ravenhill, J.R., Reid, D.S.: Thermodynamic studies of dilute aqueous solutions of cyclic ethers and simple carbohydrates. J. Solution Chem. **1**, 3–16 (1972)
7. Morel, J.P., Lhermet, C., Morel-Desrosiers, N.: Interactions between cations and sugars. 2. Enthalpies, heat-capacities, and volumes of aqueous-solutions of Ca^{2+}-d-ribose and Ca^{2+}-D-arabinose at 25 °C. Can. J. Chem. **64**, 996–1001 (1986)
8. Jasra, R.V., Ahluwalia, J.C.: Enthalpies of solution, partial molal heat capacities and apparent molal volumes of sugars and polyols in water. J. Solution Chem. **11**, 325–388 (1982)

9. Shahidi, F., Farrell, P.G., Edward, J.T.: Partial molar volumes of organic compounds in water. III. Carbohydrates. J. Solution Chem. **5**, 807–816 (1976)
10. Uedaira, H., Uedaira, H.: Diffusion coefficients of xylose and maltose in aqueous solution. Bull. Chem. Soc. Japan. **42**(8), 2140- (1969)
11. Neal, J.L., Goring, D.A.I.: Volume-temperature relationships of hydrophobic and hydrophilic nonelectrolytes in water. J. Phys. Chem. **74**, 658 (1970)
12. Longsworth, L.G.: in Electrochemistry in Biology and Medicine, ed. T. Shedlovsky, Wiley, New York (1955), Chap. 12
13. Savage, J.J.: The Enthalpy of Interaction of Non-electrolyte Pairs in Dilute Aqueous Solutions, Special Publication ARCSLSP – 77073; Department of the Army, Aberdeen, MD (1977)
14. Miyajima, K., Sawada, M., Nakagaki, M.: Studies on aqueous-solutions of saccharides. 2. Viscosity B-coefficients, apparent molar volumes, and activity-coefficients of D-glucose, maltose and maltotriose in aqueous-solutions. Bull. Chem. Soc. Jpn. **56**, 1954–1957 (1983)
15. Neal, J.L., Goring, D.A.I.: Hydrophobic folding of maltose in aqueous solution. Can. J. Chem. **48**, 3745–3747 (1970)
16. Kiyosawa, K.: The volumes of hydrated glucose, sucrose and raffinose molecules, and the osmotic pressures of these aqueous saccharide solutions as measured by the freezing-point depression method. Bull. Chem. Soc. Jpn. **61**, 633–642 (1988)
17. Bernal, P.J., van Hook, W.A.: Apparent molar volumes, isobaric expansion coefficients, and isentropic compressibilities, and their H/D isotope effects for some aqueous carbohydrate solutions. J. Chem. Thermodyn. **18**, 955–968 (1986)
18. Kishore, N., Goldberg, R.N., Tewari, Y.B.: Apparent molar heat-capacities and apparent molar volumes of aqueous glucose at temperatures from from 298.15 K to 327.01 K. J. Chem. Thermodyn. **25**, 847–859 (1993)
19. Fucaloro, A., Zanella, A., Widjaja, S., Widjaja, J.: Partial molar volumes and refractions of cobalt(III) complexes, Part 1: Homologous series of hexaaminecobalt(III) complexes J. Solution Chem. **34**, 1357–1370 (2005)
20. Bevan-Ott, J., Boerio-Goates, J.: Chemical Thermodynamics: Principles and Applications. Academic Press, London (2000), p. 209
21. Fucaloro, A.F.: Reporting molar refractions. J. Solution Chem. **31**, 601–605 (2002)
22. Fucaloro, A.F.: Partial molar volumes from refractive index measurements. J. Chem. Ed. **79**, 865–868 (2002)
23. Millero, F.J.: Partial Molar Volumes of Electrolytes in Aqueous Solutions, in Water and Aqueous Solutions: Structure, Thermodynamics, and Transport Properties. R. A. Horne, ed. Wiley-Interscience, New York (1972), p. 548
24. Vogel, A.I.: Physical properties and chemical constitution. XXIIII. Miscellaneous compounds. Investigation of the so-called co.ovrddot.ordinate or dative link in esters of oxy acids and in nitro paraffins by molecular refractivity determinations. Atomic, structural, and group parachors and refractivities. J. Chem. Soc. 1833–1855 (1948) and references cited therein