


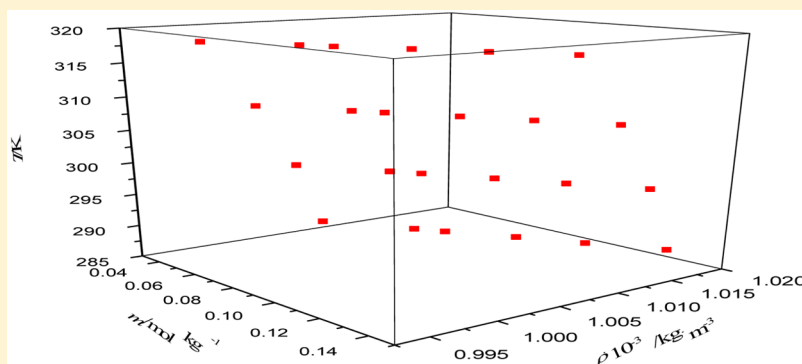
Volumetric Properties of Disaccharides in Aqueous Solutions of Benzyldimethylammonium Acetate as a Function of Temperature

Vickramjeet Singh,[†] Parampaul K. Banipal,[†] Tarlok S. Banipal,^{*,†} and Ramesh L. Gardas[‡]

[†]Department of Chemistry, Guru Nanak Dev University, Amritsar 143005, India

[‡]Department of Chemistry, Indian Institute of Technology, Madras, Chennai 600036, India

 Supporting Information



ABSTRACT: Densities, ρ , and speeds of sound, u , of two disaccharides (D-(+)-maltose and D-(+)-cellobiose) in water and in the presence of protic ionic liquid (PIL) (i.e., benzyldimethylammonium acetate, BDMAAc) were measured at different temperatures (288.15–318.15) K at atmospheric pressure. These data were used to calculate the apparent molar volume, apparent molar isentropic compressibility, infinite dilution partial molar volume, infinite dilution partial molar isentropic compressibility, and corresponding transfer parameters ($\Delta_t V^\circ_2$ and $\Delta_t K^\circ_{s,2}$) for disaccharides from water to aqueous PIL solutions. The effect of BDMAAc on the basic taste quality of disaccharides was evaluated from apparent specific volume and apparent specific isentropic compressibility, as these parameters are grouped in various taste qualities.

1. INTRODUCTION

Ionic liquids (ILs) are considered a “green benign” solvent due to their unique physicochemical properties, such as high thermal and chemical stability, low vapor pressure, high conductivity, high solvation capacity, and wide electrochemical window.^{1–3} Because of these unique properties, ILs are being employed in a number of applications, such as in chemical synthesis, catalysis, as a replacement solvent for currently used volatile organic solvents in various industrial processes, polymer chemistry, nanotechnology and as a solvent for biomass treatment.^{4–7}

Biomass is considered to be the most suitable replacement for diminishing fossil fuels, as biomass can be used to produce green energy (biodiesel) and various other useful products (biocomposites and other biocompatible materials).⁸ Research on finding an efficient route for the conversion of biomass and biopolymers (chitin, starch, cellulose, chitosan, etc.) into biocomposites and various biodegradable materials is associated with finding a better solvent for their dissolution.^{9–11} Among these biopolymers, cellulose is the favorite, as it is nonedible and available on a large scale from biomass. Because the highly ordered structure of cellulose has numerous inter- and intramolecular hydrogen bonds, it is extremely difficult to find a better solvent for its dissolution. Nowadays, a number of

ILs have been used for biomass treatment, particularly for the dissolution and chemical modification of lignocellulosic biomass.^{12,13}

The strength and nature of interactions occurring between ILs and monomer units (such as glucose, cellobiose, sucrose, etc.) of these biopolymers have also been studied.^{14–21} These studies deal mostly with volumetric properties of saccharides in the presence of imidazolium based ILs^{14–18,20,21} at 298.15 K with a few reports in which ammonium-based ILs^{19,22} containing aliphatic cationic moieties have been used. The hydrolysis of cellobiose in the presence of an IL has been studied^{23–25} both experimentally and theoretically, and it has been reported^{3,24} that both cationic and anionic parts of the IL play an important role in the hydrolysis of cellobiose. These thermodynamic properties are further helpful in the effective use of the IL in biomass treatment as well as for the design of aqueous biphasic systems composed of ILs and saccharides.^{15,20}

Ammonium-based ILs have been employed for various applications as a solvent for the dissolution of polymers and biopolymers²⁶ and also in drug delivery.²⁷ Furthermore, it has

Received: December 27, 2014

Accepted: April 28, 2015

Published: May 6, 2015

also been reported²⁸ that ILs containing acetate anions are promising solvents for biomass dissolution. In the present work, the solvation behavior of two disaccharides (cellobiose and maltose) containing the same subunits (glucose) but attached through a different glycosidic linkage ($\alpha 1 \rightarrow 4$ or $\beta 1 \rightarrow 4$) is studied in the presence of benzyldimethylammonium acetate (BDMAAc) at different temperatures (288.15 to 318.15) K at atmospheric pressure. BDMAAc is composed of aromatic cations and acetate anions; thus, it will be interesting to study the effect of BDMAAc on the volumetric properties of disaccharides. Furthermore, the strength of molecular interactions prevailing in our ternary system (disaccharides + water + BDMAAc) is discussed on the basis of various parameters calculated from the density, ρ , and speed of sound, u , data.

2. EXPERIMENTAL SECTION

2.1. Materials. Specifications of the chemicals used in the present work are given in Table 1. All of the commercially

Table 1. Specifications of Chemicals Used

chemical	source	mass fraction purity	CAS number
D-(+)-cellobiose	Sigma-Aldrich	>0.98 ^a	528-50-7
D-(+)-maltose monohydrate	Sigma-Aldrich	>0.95 ^a	6363-53-7
benzyldimethylamine	Sigma-Aldrich	>0.99 ^a	103-83-3
acetic acid	Merck	>0.99 ^a	64-19-7
benzyldimethylammonium acetate	synthesized in laboratory	>0.99 ^b	

^aPurity reported from manufacturers, and these chemicals were used without further purification. ^bPurity was validated by ¹H and ¹³C NMR spectroscopic techniques.

available chemicals were used as such without further purification. Disaccharides were used after drying in a vacuum desiccator at room temperature for 48 h.

2.2. Synthesis and Characterization of Benzyldimethylammonium Acetate. BDMAAc was synthesized²⁹ according to the method reported by Anouti et al.³⁰ Benzyldimethylamine was placed in a two-necked round-bottomed flask, immersed in an ice-bath, and equipped with a reflux condenser, dropping funnel (to add the acid), and thermometer. Under vigorous stirring, acid was added dropwise to the base (amine). Because the acid–base neutralization reaction is highly exothermic, the temperature was maintained below 278.15 K. The reaction mixture was stirred continuously for 24 h at ambient temperature, and a viscous liquid was obtained. The residual amine and/or acid were evaporated under high vacuum, and the remaining liquid was further dried in a vacuum at 323.15 K for 2 days and then stored under a nitrogen atmosphere.

The synthesized protic ionic liquid (PIL) was characterized by ¹H NMR, ¹³C NMR, and FTIR spectroscopic techniques. The ¹H and ¹³C NMR of synthesized PIL was recorded on a Bruker Avance 500 MHz spectrometer using CDCl₃ as the solvent and TMS as the internal standard. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer.

¹H NMR Analysis. (CDCl₃) δ 7.372–7.304 (m, 5H), 6.989 (broad, 1H), 3.720 (s, 2H), 2.390 (s, 6H), 2.027 (s, 3H).

¹³C NMR Analysis. (CDCl₃) δ 176.265 (C=O), 134.506, 130.158, 128.650, and 128.271 (benzene ring carbons), 62.420 (CH₂–N), 43.334, and 22.252 (saturated carbons).

IR Analysis. Characteristic peaks were found for N–H stretching at 3035 cm^{−1}, N–H bending at 1588 cm^{−1}, =C–H stretching at 2940 cm^{−1}, =C–H bending at 703 cm^{−1}, C–H stretching (for N–CH₃) at 2776 cm^{−1}, C–H bending (for CH₃) at 1462 cm^{−1}, C=O stretching at 1714 cm^{−1}.

The water content (\approx 2506 ppm) of the synthesized PIL was measured using an Analab Karl Fischer Titrator (Micro AquaCal100). The amount of water present in the PIL has been taken into account for the molality correction of stock solutions (water + PIL).

2.3. Apparatus and Procedure. Density measurements were carried out using a vibrating-tube digital densimeter (model DMA 60/602 Anton Paar, Austria). The densimeter cell was thermostated using an efficient constant temperature bath (Julabo F25/Germany) having stability within \pm 0.01 K. The densimeter was calibrated with pure water and dry air. Density measurements were made relative to pure water. The density of pure water has been taken from the literature.³¹ The standard uncertainty in the measured densities on average is 3.7·10^{−3} kg·m^{−3}. However, after considering³² the amount of impurity present in the studied samples, the standard uncertainty in density will be on the order of 2 kg·m^{−3}.

Speeds of sound, u , were determined using a multifrequency ultrasonic interferometer (model M-81, 3 MHz, Mittal Enterprises, New Delhi). The instrument was calibrated by measuring the speed of sound in double distilled freshly degassed water at different temperatures. The determined u values in water at $T = (288.15, 298.15, 308.15, \text{ and } 318.15)$ K are (1465.88, 1496.51, 1519.90, and 1536.68) m·s^{−1}, respectively, which agree well with literature values.³³ The average of at least ten readings was taken as a final value of the speed of sound. The standard uncertainty in the speed of sound is 0.50 m·s^{−1}. An efficient constant temperature bath (Julabo F25/Germany) having stability within \pm 0.01 K was used to control the temperature of the solution in a double walled cell.

The solutions were made fresh on a mass basis in airtight glass vials using a Mettler-Toledo balance (AB 265S) with a precision of \pm 0.01 mg. Deionized, doubly distilled, and freshly degassed water was used for making solutions.

3. RESULTS AND DISCUSSION

Apparent molar volumes, $V_{2,\phi}$, and apparent molar isentropic compressibilities, $K_{s,2,\phi}$, of D-(+)-cellobiose (Cel) and D-(+)-maltose monohydrate (Mal) in water and in aqueous BDMAAc solutions at different temperatures at atmospheric pressure (Table 2) were evaluated from experimentally determined density, ρ , and speed of sound, u , data using the following equations

$$V_{2,\phi} = [M/\rho] - [(\rho - \rho_0)/(m \cdot \rho \cdot \rho_0)] \quad (1)$$

$$K_{s,2,\phi} = (\kappa_s \cdot M/\rho) - [(\kappa_s^\circ \cdot \rho - \kappa_s \cdot \rho_0)/(m \cdot \rho \cdot \rho_0)] \quad (2)$$

where ρ_0 and ρ are the densities of solvent (water or water + BDMAAc) and ternary solutions, respectively, M and m are the molar mass and molality of the solute (Cel or Mal), respectively, and κ_s° and κ_s are the isentropic compressibilities of solvent and solution, respectively. Isentropic compressibilities, κ_s , were evaluated from experimentally determined density and speed of sound data as $\kappa_s = 1/u^2 \cdot \rho$.

The apparent molar volume, $V_{2,\phi}$, and apparent molar isentropic compressibility, $K_{s,2,\phi}$, values of Mal and Cel in water and in aqueous BDMAAc solutions increase with the concentration of solute and with the temperature of the

Table 2. Densities, ρ , Apparent Molar Volumes, $V_{2,\phi}$, Speeds of Sound, u , and Apparent Molar Isentropic Compressibilities, $K_{s,2,\phi}$, of Disaccharides in Water and in Aqueous BDMAAc Solutions at Temperatures $T = (288.15 \text{ to } 318.15) \text{ K}$ at 0.1 MPa^a

T	m_{B}^b	m^c	$\rho \cdot 10^{-3d}$	$V_{2,\phi} \cdot 10^6$	u^e	$K_{s,2,\phi} \cdot 10^{15}$
K	mol·kg ⁻¹	mol·kg ⁻¹	kg·m ⁻³	m ³ ·mol ⁻¹	m·s ⁻¹	m ³ ·mol ⁻¹ ·Pa ⁻¹
D-(+)-Cellobiose						
288.15	0.0		$\rho_o = 0.999129$		$u_0 = 1465.88$	
		0.04565	1.005093	210.47	1470.63	-34.07
		0.07217	1.008495	210.62	1473.62	-33.91
		0.08095	1.009611	210.67	1474.62	-33.90
		0.10052	1.012083	210.77	1476.85	-33.82
		0.11911	1.014407	210.88	1478.98	-33.74
0.14000		1.016995	210.99	1481.40	-33.72	
298.15			$\rho_o = 0.997049$		$u_0 = 1496.51$	
		0.04565	1.002978	211.36	1500.93	-25.63
		0.07217	1.006365	211.46	1503.68	-25.55
		0.08095	1.007477	211.49	1504.59	-25.49
		0.10052	1.009940	211.55	1506.63	-25.40
		0.11911	1.012259	211.61	1508.59	-25.39
0.14000		1.014841	211.68	1510.80	-25.35	
308.15			$\rho_o = 0.994063$		$u_0 = 1519.90$	
		0.04565	0.999945	212.69	1525.10	-19.63
		0.07217	1.003299	212.86	1527.68	-19.55
		0.08095	1.004399	212.92	1528.54	-19.52
		0.10052	1.006834	213.04	1530.47	-19.49
		0.11911	1.009130	213.10	1532.31	-19.45
0.14000		1.011680	213.22	1534.38	-19.36	
318.15			$\rho_o = 0.990244$		$u_0 = 1536.68$	
		0.04565	0.996094	213.72	1540.19	-15.62
		0.07217	0.999428	213.91	1542.63	-15.56
	0.08095	1.000522	213.97	1543.44	-15.52	
	0.10052	1.002942	214.10	1545.26	-15.46	
	0.11911	1.005221	214.20	1547.00	-15.42	
0.14000	1.007752	214.35	1548.98	-15.41		
288.15	0.05		$\rho_o = 1.000061$		$u_0 = 1482.78$	
		0.04137	1.005386	212.44	1486.71	-25.20
		0.06856	1.008833	212.48	1489.52	-25.04
		0.07664	1.009849	212.50	1490.36	-25.01
		0.10720	1.013661	212.54	1493.56	-24.99
		0.13185	1.016698	212.58	1496.15	-24.92
0.15504		1.019526	212.61	1498.60	-24.87	
298.15			$\rho_o = 0.997958$		$u_0 = 1504.54$	
		0.04137	1.003244	213.57	1507.65	-14.78
		0.06856	1.006666	213.61	1510.08	-14.71
		0.07664	1.007674	213.63	1510.81	-14.72
		0.10720	1.011457	213.67	1513.57	-14.66
		0.13185	1.014471	213.71	1515.81	-14.61
0.15504		1.017276	213.75	1517.92	-14.53	
308.15			$\rho_o = 0.995017$		$u_0 = 1526.68$	
		0.04137	1.000219	215.87	1530.38	-7.92
		0.06856	1.003586	215.92	1532.60	-7.84
		0.07664	1.004578	215.94	1533.26	-7.79
		0.10720	1.008298	216.00	1535.78	-7.73
		0.13185	1.011261	216.05	1537.84	-7.74
0.15504		1.014020	216.09	1539.77	-7.67	
318.15			$\rho_o = 0.991082$		$u_0 = 1542.62$	
		0.04137	0.996245	217.18	1545.65	-2.49
		0.06856	0.999587	217.22	1547.65	-2.42
	0.07664	1.000572	217.24	1548.25	-2.43	
	0.10720	1.004265	217.29	1550.52	-2.36	
	0.13185	1.007208	217.33	1552.36	-2.30	
0.15504	1.009946	217.37	1554.10	-2.24		
		$\rho_o = 1.001058$		$u_0 = 1491.25$		

Table 2. continued

T	m_B^b	m^c	$\rho \cdot 10^{-3}^d$	$V_{2,\phi} \cdot 10^6$	u^e	$K_{s,2,\phi} \cdot 10^{15}$
K	mol·kg ⁻¹	mol·kg ⁻¹	kg·m ⁻³	m ³ ·mol ⁻¹	m·s ⁻¹	m ³ ·mol ⁻¹ ·Pa ⁻¹
D-(+)-Cellobiose						
288.15	0.10	0.04844	1.007337	211.27	1496.85	-28.76
		0.06493	1.009442	211.31	1498.66	-28.72
		0.08801	1.012366	211.34	1501.20	-28.66
		0.11483	1.015725	211.38	1504.18	-28.63
		0.12180	1.016591	211.40	1504.95	-28.59
		0.16228	1.021574	211.45	1509.48	-28.51
298.15		$\rho_o = 0.999043$			$u_o = 1512.04$	
		0.04844	1.005249	212.95	1516.37	-18.85
		0.06493	1.007329	213.00	1517.98	-18.91
		0.08801	1.010217	213.04	1520.23	-18.86
		0.11483	1.013536	213.08	1522.86	-18.81
		0.12180	1.014391	213.10	1523.54	-18.76
308.15		0.16228	1.019311	213.17	1527.55	-18.70
		$\rho_o = 0.995871$			$u_o = 1533.24$	
		0.04844	1.002018	214.44	1537.68	-11.52
		0.06493	1.004080	214.47	1539.11	-11.46
		0.08801	1.006941	214.51	1541.13	-11.44
		0.11483	1.010230	214.54	1543.49	-11.41
318.15		0.12180	1.011076	214.57	1544.10	-11.36
		0.16228	1.015950	214.63	1547.70	-11.32
		$\rho_o = 0.991952$			$u_o = 1548.36$	
		0.04844	0.998036	216.11	1552.97	-4.73
		0.06493	1.000076	216.15	1554.24	-4.71
		0.08801	1.002907	216.19	1556.01	-4.59
		0.11483	1.006161	216.22	1558.09	-4.54
		0.12180	1.007000	216.24	1558.64	-4.56
		0.16228	1.011823	216.30	1561.81	-4.48
		$\rho_o = 1.001820$			$u_o = 1502.34$	
		0.05241	1.008645	210.50	1508.69	-30.71
		0.06799	1.010643	210.53	1510.47	-30.72
288.15	0.15	0.09529	1.014110	210.59	1513.60	-30.66
		0.12182	1.017441	210.63	1516.66	-30.60
		0.13153	1.018648	210.66	1517.79	-30.59
		0.13879	1.019548	210.68	1518.64	-30.60
		$\rho_o = 0.999682$			$u_o = 1517.72$	
		0.05241	1.006446	211.83	1523.37	-20.91
298.15		0.06799	1.008425	211.88	1524.92	-20.81
		0.09529	1.011862	211.92	1527.66	-20.77
		0.12182	1.015161	211.98	1530.34	-20.71
		0.13153	1.016358	212.01	1531.33	-20.71
		0.13879	1.017249	212.03	1532.06	-20.65
		$\rho_o = 0.996548$			$u_o = 1538.21$	
308.15		0.05241	1.003210	214.06	1543.18	-14.24
		0.06799	1.005160	214.09	1544.62	-14.25
		0.09529	1.008545	214.13	1547.15	-14.20
		0.12182	1.011795	214.18	1549.62	-14.13
		0.13153	1.012976	214.19	1550.52	-14.08
		0.13879	1.013852	214.22	1551.21	-14.09
318.15		$\rho_o = 0.992662$			$u_o = 1552.71$	
		0.05241	0.999273	215.39	1556.86	-9.61
		0.06799	1.001208	215.42	1558.19	-9.59
		0.09529	1.004567	215.46	1560.53	-9.53
		0.12182	1.007794	215.49	1562.82	-9.49
		0.13153	1.008964	215.51	1563.66	-9.46
288.15	0.20	0.13879	1.009835	215.53	1564.29	-9.44
		$\rho_o = 1.002847$			$u_o = 1512.87$	
		0.05368	1.009871	209.75	1518.51	-31.85
		0.07104	1.012106	209.79	1520.53	-31.76

Table 2. continued

T	m_B^b	m^c	$\rho \cdot 10^{-3}^d$	$V_{2,\phi} \cdot 10^6$	u^e	$K_{s,2,\phi} \cdot 10^{15}$
K	mol·kg ⁻¹	mol·kg ⁻¹	kg·m ⁻³	m ³ ·mol ⁻¹	m·s ⁻¹	m ³ ·mol ⁻¹ ·Pa ⁻¹
D-(+)-Cellobiose						
298.15		0.08947	1.014461	209.82	1522.68	-31.66
		0.11243	1.017369	209.86	1525.37	-31.56
		0.12371	1.018784	209.90	1526.70	-31.51
		0.13982	1.020796	209.93	1528.61	-31.48
		$\rho_o = 1.000712$		$u_o = 1526.72$		
		0.05368	1.007687	210.83	1531.67	-22.45
		0.07104	1.009906	210.88	1533.44	-22.32
		0.08947	1.012244	210.92	1535.34	-22.31
		0.11243	1.015130	210.96	1537.72	-22.29
		0.12371	1.016537	210.98	1538.89	-22.25
		0.13982	1.018533	211.02	1540.56	-22.17
		$\rho_o = 0.997483$		$u_o = 1545.21$		
		0.05368	1.004392	212.34	1549.98	-16.15
		0.07104	1.006590	212.38	1551.61	-16.08
308.15		0.08947	1.008906	212.41	1553.35	-16.04
		0.11243	1.011766	212.44	1555.53	-16.01
		0.12371	1.013159	212.47	1556.61	-16.00
		0.13982	1.015137	212.50	1558.15	-15.96
		$\rho_o = 0.993451$		$u_o = 1558.83$		
		0.05368	1.000315	213.52	1563.89	-11.29
		0.07104	1.002499	213.56	1565.40	-11.31
		0.08947	1.004800	213.59	1567.00	-11.25
		0.11243	1.007641	213.62	1569.00	-11.17
		0.12371	1.009025	213.65	1569.99	-11.15
		0.13982	1.010991	213.68	1571.41	-11.12
		D-(+)-Maltose Monohydrate				
		0.04928	1.005643	226.72	1471.11	-28.26
		0.08226	1.009916	226.81	1474.88	-28.17
298.15	0.0	0.08926	1.010813	226.84	1475.68	-28.11
		0.10447	1.012754	226.88	1477.43	-28.07
		0.11714	1.014360	226.91	1478.89	-28.01
		0.16144	1.019898	227.03	1484.05	-27.94
		0.04928	1.003496	228.26	1501.82	-24.86
		0.08226	1.007726	228.34	1505.59	-24.79
		0.08926	1.008615	228.36	1506.39	-24.75
		0.10447	1.010536	228.40	1508.14	-24.71
		0.11714	1.012126	228.43	1509.61	-24.71
		0.16144	1.017611	228.53	1514.75	-24.58
		0.04928	1.000452	229.79	1525.97	-18.71
		0.08226	1.004642	229.87	1529.53	-18.70
		0.08926	1.005521	229.91	1530.28	-18.61
		0.10447	1.007425	229.94	1531.93	-18.59
308.15		0.11714	1.009001	229.96	1533.30	-18.52
		0.16144	1.014431	230.07	1538.15	-18.43
		0.04928	0.996572	231.43	1541.19	-15.89
		0.08226	1.000721	231.52	1544.66	-15.81
		0.08926	1.001593	231.54	1545.40	-15.79
		0.10447	1.003476	231.60	1547.01	-15.73
		0.11714	1.005036	231.62	1548.35	-15.68
		0.16144	1.010411	231.75	1553.09	-15.59
		0.05009	1.006577	228.73	1487.64	-18.94
		0.06292	1.008220	228.76	1488.98	-18.91
		0.08558	1.011099	228.80	1491.35	-18.84
		0.09276	1.012004	228.82	1492.10	-18.79
		0.12046	1.015469	228.87	1495.03	-18.79
		0.13449	1.017206	228.90	1496.51	-18.73
298.15	0.05	0.05009	1.004386	230.71	1508.96	-13.87
		0.06292	1.006007	230.73	1510.24	-13.79

Table 2. continued

T	m_{B}^b	m^c	$\rho \cdot 10^{-3d}$	$V_{2,\phi} \cdot 10^6$	u^e	$K_{s,2,\phi} \cdot 10^{15}$	
K	mol·kg ⁻¹	mol·kg ⁻¹	kg·m ⁻³	m ³ ·mol ⁻¹	m·s ⁻¹	m ³ ·mol ⁻¹ ·Pa ⁻¹	
D-(+)-Maltose Monohydrate							
308.15	0.10	0.08558	1.008846	230.78	1512.51	-13.70	
		0.09276	1.009738	230.81	1513.23	-13.65	
		0.12046	1.013155	230.86	1516.03	-13.61	
		0.13449	1.014867	230.89	1517.45	-13.56	
		0.05009	1.001342	233.09	1531.54	-5.97	
		0.06292	1.002937	233.12	1532.70	-5.90	
		0.08558	1.005728	233.19	1534.77	-5.88	
		0.09276	1.006606	233.21	1535.42	-5.83	
		0.12046	1.009964	233.28	1537.97	-5.81	
		0.13449	1.011647	233.32	1539.26	-5.76	
318.15		0.05009	0.997324	235.20	1546.95	-2.23	
		0.06292	0.998898	235.23	1548.06	-2.17	
		0.08558	1.001654	235.27	1550.03	-2.10	
		0.09276	1.002521	235.29	1550.65	-2.05	
		0.12046	1.005836	235.35	1553.08	-2.01	
		0.13449	1.007499	235.38	1554.30	-1.93	
		288.15	0.04836	1.007381	228.01	1496.82	-21.58
			0.07442	1.010727	228.07	1499.66	-21.45
			0.09088	1.012819	228.11	1501.46	-21.38
			0.10746	1.014909	228.15	1503.28	-21.31
0.13488			1.018328	228.22	1506.32	-21.28	
0.15469			1.020771	228.27	1508.52	-21.22	
298.15			0.04836	1.005276	230.09	1516.80	-17.00
			0.07442	1.008574	230.15	1519.56	-16.92
			0.09088	1.010635	230.19	1521.31	-16.87
			0.10746	1.012693	230.24	1523.09	-16.86
		0.13488	1.016063	230.30	1526.03	-16.78	
		0.15469	1.018470	230.35	1528.17	-16.75	
		308.15	0.04836	1.002025	232.06	1538.16	-9.67
			0.07442	1.005281	232.11	1540.68	-9.55
			0.09088	1.007316	232.15	1542.29	-9.56
			0.10746	1.009350	232.19	1543.90	-9.46
0.13488			1.012677	232.25	1546.59	-9.40	
0.15469			1.015054	232.29	1548.55	-9.38	
318.15			0.04836	0.998025	234.18	1553.67	-5.17
			0.07442	1.001237	234.24	1556.05	-5.08
			0.09088	1.003246	234.27	1557.56	-5.04
			0.10746	1.005252	234.31	1559.09	-5.01
		0.13488	1.008534	234.37	1561.62	-4.92	
		0.15469	1.010879	234.41	1563.46	-4.88	
		288.15	0.04096	1.007214	227.22	1507.35	-23.33
			0.07588	1.011728	227.31	1511.29	-23.27
			0.09222	1.013814	227.35	1513.14	-23.20
			0.10025	1.014832	227.38	1514.06	-23.21
0.11246			1.016375	227.40	1515.44	-23.12	
0.15560			1.021750	227.51	1520.39	-23.03	
298.15			0.04096	1.005013	228.96	1522.60	-19.03
			0.07588	1.009476	229.02	1526.40	-18.97
			0.09222	1.011539	229.05	1528.19	-18.95
			0.10025	1.012547	229.07	1529.07	-18.93
		0.11246	1.014072	229.09	1530.41	-18.89	
		0.15560	1.019391	229.16	1535.17	-18.77	
		308.15	0.04096	1.001798	231.27	1542.46	-11.79
			0.07588	1.006191	231.36	1545.95	-11.67
			0.09222	1.008220	231.40	1547.59	-11.61
			0.10025	1.009207	231.47	1548.40	-11.55
0.11246			1.010706	231.50	1549.64	-11.55	
0.15560			1.015931	231.62	1554.03	-11.46	

Table 2. continued

T	m_B^b	m^c	$\rho \cdot 10^{-3d}$	$V_{2,\phi} \cdot 10^6$	u^e	$K_{s,2,\phi} \cdot 10^{15}$
K	mol·kg ⁻¹	mol·kg ⁻¹	kg·m ⁻³	m ³ ·mol ⁻¹	m·s ⁻¹	m ³ ·mol ⁻¹ ·Pa ⁻¹
D-(+)-Maltose Monohydrate						
318.15	0.20	0.04096	0.997853	233.14	1556.31	-7.99
		0.07588	1.002197	233.21	1559.64	-7.86
		0.09222	1.004204	233.25	1561.21	-7.83
		0.10025	1.005184	233.27	1561.98	-7.79
		0.11246	1.006667	233.30	1563.15	-7.73
0.15560		1.011841	233.38	1567.31	-7.58	
288.15		0.05739	1.010396	226.79	1518.95	-24.96
		0.07539	1.012721	226.83	1521.05	-24.89
		0.08920	1.014491	226.86	1522.67	-24.87
		0.10390	1.016362	226.89	1524.39	-24.78
		0.12952	1.019593	226.94	1527.41	-24.70
298.15		0.14819	1.021922	226.98	1529.61	-24.61
		0.05739	1.008174	228.52	1532.65	-20.89
		0.07539	1.010470	228.57	1534.69	-20.87
		0.08920	1.012219	228.61	1536.26	-20.85
		0.10390	1.014067	228.65	1537.93	-20.78
308.15		0.12952	1.017259	228.70	1540.87	-20.78
		0.14819	1.019560	228.74	1543.01	-20.71
		0.05739	1.004867	230.20	1550.84	-13.61
		0.07539	1.007140	230.25	1552.70	-13.60
		0.08920	1.008871	230.28	1554.13	-13.58
318.15		0.10390	1.010701	230.31	1555.65	-13.52
		0.12952	1.013858	230.37	1558.32	-13.47
		0.14819	1.016135	230.41	1560.28	-13.45
		0.05739	1.000750	232.11	1564.94	-10.22
		0.07539	1.002997	232.16	1566.72	-10.13
		0.08920	1.004705	232.22	1568.10	-10.10
		0.10390	1.006510	232.28	1569.57	-10.05
		0.12952	1.009627	232.36	1572.15	-10.02
		0.14819	1.011873	232.42	1574.03	-9.96

^aThe standard uncertainties are $u(T) = 0.01$ K, $u(m) = 2.35 \cdot 10^{-6}$ mol·kg⁻¹, $u(\rho) = 2$ kg·m⁻³, $u(u) = 0.50$ m·s⁻¹, $u(P) = 0.50$ kPa. The combined uncertainties, U , are $U(V_\phi) = (0.14 \text{ to } 0.06) \cdot 10^{-6}$ m³·mol⁻¹ and $U(K_{s,2,\phi}) = (0.90 \text{ to } 0.40) \cdot 10^{-15}$ m³·mol⁻¹·Pa⁻¹ for the low and high concentration range of disaccharides, respectively ($k \approx 2$, level of confidence = 0.95). m_B is the molality of BDMAAc in water. m is the molality of disaccharides in water or water + BDMAAc solutions. ρ_o is the density of BDMAAc in water. u_o is the speed of sound of BDMAAc in water.

solution. The variation of $V_{2,\phi}$ values versus molality, m , of Cel in 0.10 mol·kg⁻¹ aqueous BDMAAc solutions at different temperatures is shown in Figure 1. The combined uncertainties in $V_{2,\phi}$ values resulting from various quantities ranges from $(0.06 \text{ to } 0.14) \cdot 10^{-6}$ m³·mol⁻¹ at low (≤ 0.05 mol·kg⁻¹) and high concentration ranges of disaccharides, respectively, and combined uncertainties in $K_{s,2,\phi}$ values range from $(0.40 \text{ to } 0.90) \cdot 10^{-15}$ m³·mol⁻¹·Pa⁻¹ ($k \approx 2$, level of confidence = 0.95).

Partial molar volumes ($V_2^\circ = V_{2,\phi}^\circ$) and partial molar isentropic compressibilities ($K_{s,2}^\circ = K_{s,2,\phi}^\circ$) at infinite dilution were determined by least-squares fitting of the following relation to $V_{2,\phi}$ and $K_{s,2,\phi}$ data as

$$V_{2,\phi} = V_2^\circ + S_v \cdot m \quad (3)$$

$$K_{s,2,\phi} = K_{s,2}^\circ + S_K \cdot m \quad (4)$$

where S_v and S_K are experimental slopes, respectively. Partial molar volumes at infinite dilution (V_2° and $K_{s,2}^\circ$) of Mal and Cel in water at different temperatures agree well with literature values^{34–40} (Tables 3 and 4). The information regarding solute-solvent interactions in ternary solutions may be obtained from the dependence of the infinite dilution partial molar property on temperature, as at infinite dilution the solute-solute

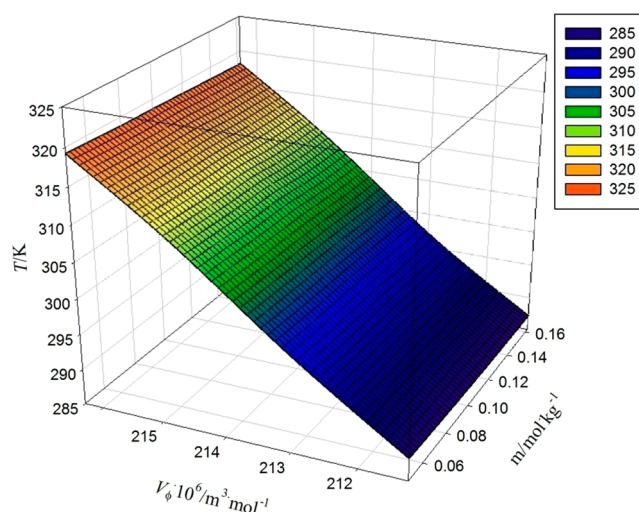


Figure 1. Plot of apparent molar volumes, V_ϕ , versus molalities, m , of D-(+)-cellobiose in 0.10 mol·kg⁻¹ BDMAAc solution at temperatures $T = (288.15, 298.15, 308.15, \text{ and } 318.15)$ K.

interactions become negligible. The V_2° and $K_{s,2}^\circ$ values of disaccharides in the presence of BDMAAc increase with

Table 3. Standard Partial Molar Volumes at Infinite Dilution, V°_2 , of Disaccharides in Water and in Aqueous BDMAAc Solutions at $T = (288.15 \text{ to } 318.15) \text{ K}$ at 0.1 MPa

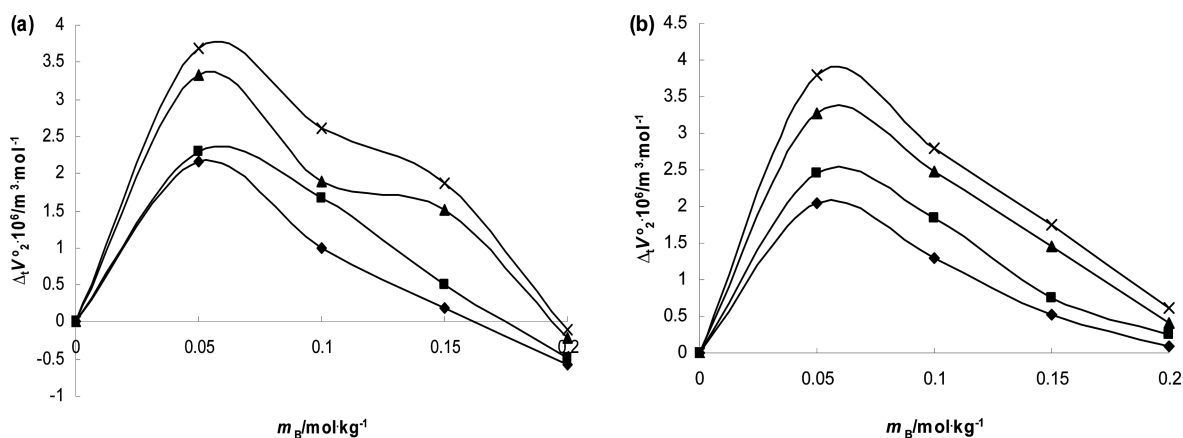
m_B^a mol·kg ⁻¹	$V^\circ_2 \cdot 10^6 \text{ m}^3 \cdot \text{mol}^{-1}$			
	288.15 K	298.15 K	308.15 K	318.15 K
D-(+)-Cellobiose				
0.00	210.22 ± 0.01 ^b (5.51) ^c [210.18 ^d , 210.17 ^e , 210.21 ^f , 210.29 ^g]	211.21 ± 0.01 (3.34) [211.29 ^d , 211.31 ^{e,f} , 211.43 ^g , 211.98 ^h]	212.46 ± 0.02 (5.52) [212.37 ^d , 212.42 ^{e,f} , 212.55 ^g , 213.58 ^h]	213.43 ± 0.01 (6.57) [213.51 ^d , 213.52 ^e , 213.54 ^f , 213.65 ^g , 214.90 ^h]
0.05	212.38 ± 0.01 (1.50)	213.51 ± 0.01 (1.57)	215.79 ± 0.01 (1.96)	217.11 ± 0.01 (1.68)
0.10	211.20 ± 0.01 (1.56)	212.87 ± 0.01 (1.86)	214.36 ± 0.01 (1.65)	216.04 ± 0.01 (1.62)
0.15	210.39 ± 0.01 (2.06)	211.72 ± 0.01 (2.20)	213.97 ± 0.01 (1.75)	215.32 ± 0.01 (1.51)
0.20	209.64 ± 0.01 (2.09)	210.72 ± 0.01 (2.11)	212.25 ± 0.01 (1.79)	213.43 ± 0.01 (1.79)
D-(+)-Maltose Monohydrate				
0.00	226.59 ± 0.01 ^b (2.76) ^c [226.57 ^d , 226.55 ^e , 226.60 ^f , 226.66 ^g]	228.14 ± 0.01 (2.42) [228.08 ^d , 228.12 ^e , 228.14 ^f , 228.20 ^g]	229.67 ± 0.01 (4.48) [229.70 ^{d,f} , 229.73 ^e , 229.77 ^g]	231.29 ± 0.01 (2.87) [231.30 ^{d,f} , 230.31 ^e , 231.20 ^g]
0.05	228.63 ± 0.01 (1.94)	230.60 ± 0.01 (2.18)	232.95 ± 0.01 (2.74)	235.09 ± 0.01 (2.12)
0.10	227.89 ± 0.01 (2.45)	229.97 ± 0.01 (2.46)	231.95 ± 0.01 (2.22)	234.08 ± 0.01 (2.17)
0.15	227.12 ± 0.01 (2.53)	228.89 ± 0.01 (1.76)	231.13 ± 0.01 (3.15)	233.05 ± 0.01 (2.11)
0.20	226.67 ± 0.01 (2.07)	228.39 ± 0.01 (2.41)	230.07 ± 0.01 (2.28)	231.91 ± 0.01 (3.49)

^a m_B is the molality of BDMAAc in water. ^bStandard deviation. ^c S_v in $\text{m}^3 \cdot \text{kg} \cdot \text{mol}^{-2}$. ^dFrom ref 34. ^eFrom ref 35. ^fFrom ref 36. ^gFrom ref 37. ^hFrom ref 38.

Table 4. Partial Molar Isentropic Compressibilities at Infinite Dilution, $K^\circ_{s,2}$, of Disaccharides in Water and in Aqueous Solutions of BDMAAc at Temperatures $T = (288.15 \text{ to } 318.15) \text{ K}$ at 0.1 MPa

m_B^a mol·kg ⁻¹	$K^\circ_{s,2} \cdot 10^{-15} \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}$			
	288.15 K	298.15 K	308.15 K	318.15 K
D-(+)-Cellobiose				
0.0	-34.20 ± 0.03 ^b (3.72) ^c [-34.27 ^d]	-25.75 ± 0.03 (3.08) [-25.81 ^d , -25.00 ^e]	-19.75 ± 0.01 (2.67) [-19.71 ^d]	-15.72 ± 0.02 (2.39) [-15.66 ^d]
0.05	-25.25 ± 0.04 (2.54)	-14.87 ± 0.01 (2.07)	-7.97 ± 0.03 (2.00)	-2.58 ± 0.01 (2.15)
0.10	-28.86 ± 0.06 (2.16)	-18.98 ± 0.04 (1.01)	-11.59 ± 0.02 (1.68)	-4.83 ± 0.03 (2.29)
0.15	-30.81 ± 0.02 (1.60)	-21.01 ± 0.03 (2.50)	-14.37 ± 0.02 (2.04)	-9.72 ± 0.01 (1.95)
0.20	-32.07 ± 0.02 (4.44)	-22.56 ± 0.04 (2.63)	-16.24 ± 0.02 (2.00)	-11.44 ± 0.02 (2.32)
D-(+)-Maltose Monohydrate				
0.0	-28.39 ± 0.03 ^b (2.95) ^c [-28.33 ^d]	-24.98 ± 0.02 (2.47) [-25.00 ^d]	-18.87 ± 0.04 (2.72) [-18.85 ^d]	-16.03 ± 0.01 (2.78) [-16.04 ^d]
0.05	-19.05 ± 0.02 (2.36)	-14.01 ± 0.03 (3.48)	-6.06 ± 0.02 (2.21)	-2.38 ± 0.02 (3.31)
0.10	-21.70 ± 0.01 (3.24)	-17.10 ± 0.01 (2.31)	-9.78 ± 0.03 (2.74)	-5.29 ± 0.01 (2.70)
0.15	-23.46 ± 0.02 (2.74)	-19.14 ± 0.02 (2.27)	-11.89 ± 0.03 (2.92)	-8.14 ± 0.01 (3.58)
0.20	-25.19 ± 0.02 (3.83)	-21.01 ± 0.02 (1.94)	-13.74 ± 0.02 (1.98)	-10.34 ± 0.02 (2.63)

^a m_B is the molality of BDMAAc in water. ^bStandard deviation. ^c S_v in $\text{m}^3 \cdot \text{kg} \cdot \text{Pa}^{-1}$. ^dFrom ref 39. ^eFrom ref 40.

**Figure 2.** Plots of partial molar volumes of transfer, ΔV°_2 , versus molalities, m_B , of BDMAAc of (a) Cel and (b) Mal at temperatures $T = 288.15 \text{ K}$ (◆), 298.15 K (■), 308.15 K (▲), and 318.15 K (×).

concentration of BDMAAc up to $m_B \approx 0.05 \text{ mol} \cdot \text{kg}^{-1}$; thereafter, V°_2 values decrease with PIL concentration.

However, in the presence of 1-allyl-3-methylimidazolium chloride¹⁶ and 1-butyl-3-methylimidazolium tetrafluorobo-

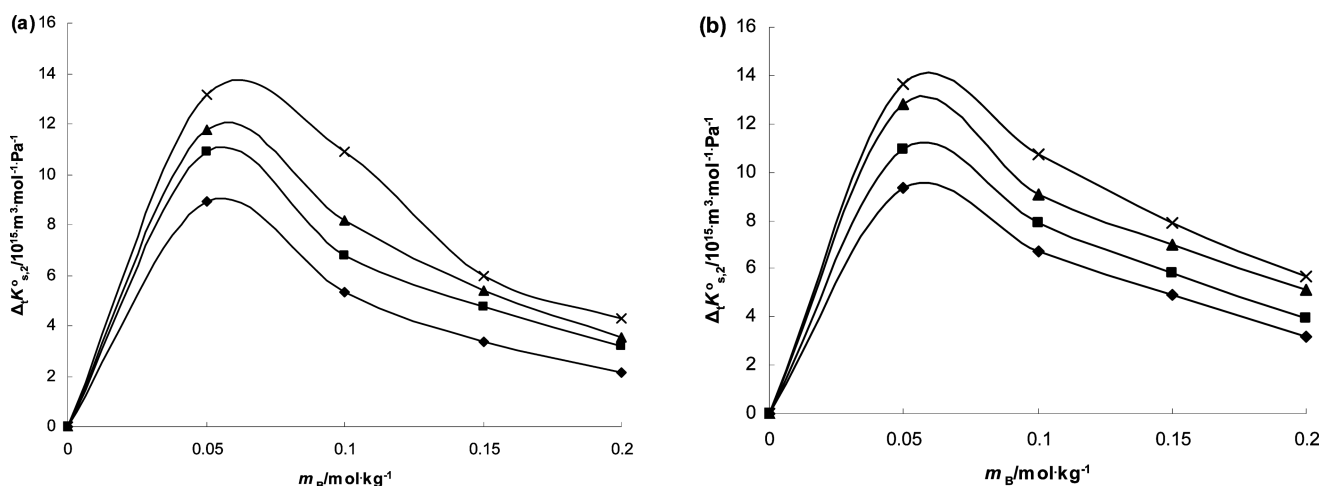


Figure 3. Plots of partial molar isentropic compressibilities of transfer, $\Delta_t K_{s,2}^\circ$, versus molalities, m_B , of BDMAAc of (a) Cel and (b) Mal at temperatures $T = 288.15$ K (\blacklozenge), 298.15 K (\blacksquare), 308.15 K (\blacktriangle), and 318.15 K (\times).

rate,²¹ an increase in the V_2° values of disaccharide (sucrose) with the concentration of IL has been reported. The $K_{s,2}^\circ$ values for disaccharides in water and in the presence of BDMAAc are negative, which become less negative with increasing concentration of BDMAAc. Further, the Kirkwood model^{41,42} can be used to explain $K_{s,2}^\circ$ values, according to which the bulk water has an open structure compared to electrostricted water and is thus more compressible. Upon the addition of BDMAAc, electrostricted water becomes more like bulk water and this results in higher $K_{s,2}^\circ$ values for disaccharides in aqueous solutions of BDMAAc compared to their values in water.

Partial molar volumes of transfer, $\Delta_t V_2^\circ$, and partial molar isentropic compressibilities of transfer, $\Delta_t K_{s,2}^\circ$, for Mal and Cel from water to aqueous BDMAAc solutions were calculated using the following equation

$$\Delta_t X_2^\circ = X_2^\circ(\text{in aqueous solutions of BDMAAc}) - X_2^\circ(\text{in water}) \quad (5)$$

where $X_2^\circ = (V_2^\circ \text{ or } K_{s,2}^\circ)$, $\Delta_t X_2^\circ = (\Delta_t V_2^\circ \text{ or } \Delta_t K_{s,2}^\circ)$. The $\Delta_t V_2^\circ$ values were found to be positive for Mal, whereas both positive and negative $\Delta_t V_2^\circ$ values have been observed in the case of Cel. The $\Delta_t K_{s,2}^\circ$ values are found to be positive for both disaccharides. The $\Delta_t V_2^\circ$ (Figures 2 a and b) and $\Delta_t K_{s,2}^\circ$ values (Figures 3 a and b) first increase with concentration of BDMAAc up to $m_B \approx 0.06 \text{ mol}\cdot\text{kg}^{-1}$; thereafter, both transfer parameters ($\Delta_t V_2^\circ$ and $\Delta_t K_{s,2}^\circ$) decrease with concentration of BDMAAc at all temperatures. The $\Delta_t V_2^\circ$ values for Cel become negative at higher concentrations of BDMAAc depending upon the temperature.

In the presence of PILs containing an aliphatic cationic moiety [3-hydroxypropylammonium formate (3-HPAF) and 3-hydroxypropylammonium acetate (3-HPAAC)], positive $\Delta_t V_2^\circ$ and $\Delta_t K_{s,2}^\circ$ values for saccharides have been observed^{19,22} at studied temperatures and concentrations of PILs; whereas in the present study, the $\Delta_t V_2^\circ$ values for Cel are negative at a higher concentration of BDMAAc (containing an aromatic cationic moiety). Jin and Chen^{15,16} reported a positive magnitude of $\Delta_t V_2^\circ$ for monosaccharide (glucose) in aqueous 1-butyl-3-methylimidazolium tetrafluoroborate and also for disaccharide (sucrose) in aqueous 1-allyl-3-methylimidazolium chloride solutions, suggesting the dominance of hydrophilic-ionic interactions between the cations and hydrophilic sites ($-\text{OH}$, $-\text{C}=\text{O}$, and $-\text{O}-$) of sucrose. Similarly, Wu et al.²²

have also reported a positive magnitude of $\Delta_t V_2^\circ$ values of sucrose in aqueous 1-butyl-3-methylimidazolium tetrafluoroborate solutions at 298.15 K. Positive $\Delta_t V_2^\circ$ values for saccharides were also observed^{17,20} in the presence of various other imidazolium-based ILs, and the strength of the interactions between the saccharide and the IL was found to increase with the concentration of IL as well as with the alkyl chain length. In most of these cases,^{15–17,20,22} an increase in $\Delta_t V_2^\circ$ values with concentration of IL has been reported; whereas in the present study, a decrease was observed (only after $m_B \approx 0.06 \text{ mol}\cdot\text{kg}^{-1}$ of PIL). Overall, the transfer volumes ($\Delta_t V_2^\circ$ or $\Delta_t K_{s,2}^\circ$) were found to be higher in the case of Mal than for Cel, which suggest that Mal containing a flexible $\alpha 1 \rightarrow 4$ glycosidic bond interacts strongly with PIL in comparison to Cel containing a $\beta 1 \rightarrow 4$ glycosidic bond. The stereochemical effects of different glycosidic bonds present in Mal and Cel have also been observed in the presence of various cosolutes.^{34,36}

The variation of V_2° with temperature can be expressed as

$$V_2^\circ = a + bT + cT^2 \quad (6)$$

where a , b , and c are the empirical parameters. The expansion coefficient, $(\partial V_2^\circ / \partial T)_P$, and the second derivative, $(\partial^2 V_2^\circ / \partial T^2)_P$, (Table S1 of the Supporting Information) were calculated by differentiating eq 6 with respect to temperature at constant pressure. The $(\partial V_2^\circ / \partial T)_P$ values for Cel in water decrease whereas $(\partial V_2^\circ / \partial T)_P$ values increase with temperature in aqueous BDMAAc solutions, and in case of Mal, $(\partial V_2^\circ / \partial T)_P$ values increase with temperature both in aqueous and mixed aqueous solutions (Table 5). Because of the small set of temperatures studied, detailed discussion of the second derivative, $(\partial^2 V_2^\circ / \partial T^2)_P$, is not given.

Hydration numbers, N_w , were also calculated for Mal and Cel in water and in the presence of BDMAAc using the method reported by Millero, Antonio, and Charles⁴³ as

$$N_w = -[K_{s,2}^\circ(\text{elect}) / (K_s^\circ \cdot V_1^\circ)] \quad (7)$$

where V_1° is the molar volume of bulk water or bulk solvent, K_s° is the compressibility of bulk water or bulk solvent, and $K_{s,2}^\circ(\text{elect})$ is the electrostriction partial molar compressibility. The electrostriction partial molar compressibility is the pressure derivative of electrostriction partial molar volume⁴⁴ and is represented as $K_{s,2}^\circ(\text{elect}) = -(\partial V_2^\circ(\text{elect}) / \partial P)$. The $K_{s,2}^\circ(\text{elect})$ values have been calculated using the equation

Table 5. Partial Molar Expansion Coefficients, $(\partial V_2^\circ/\partial T)_P$, of Disaccharides in Water and in Aqueous BDMAAc Solutions at Temperatures $T = (288.15 \text{ to } 318.15) \text{ K}$ at 0.1 MPa

m_B mol·kg ⁻¹	$(\partial V_2^\circ/\partial T)_P \cdot 10^6 \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$				
	288.15 K	298.15 K	308.15 K	318.15 K	SD ^a
D-(+)-Cellobiose					
0.00	0.110	0.109	0.108	0.107	0.121
0.05	0.150	0.160	0.169	0.179	0.471
0.10	0.159	0.160	0.160	0.161	0.025
0.15	0.169	0.170	0.171	0.172	0.407
0.20	0.122	0.127	0.132	0.137	0.201
D-(+)-Maltose Monohydrate					
0.00	0.151	0.155	0.158	0.162	0.025
0.05	0.205	0.213	0.222	0.230	0.132
0.10	0.202	0.204	0.207	0.209	0.056
0.15	0.189	0.197	0.204	0.212	0.177
0.20	0.165	0.171	0.177	0.183	0.045

^aSD = standard deviation.

$$K_{s,2}^{\circ}(\text{elect}) = K_s^{\circ}(\text{solute}) - K^{\circ}(\text{int}) \quad (8)$$

where $K^{\circ}(\text{int})$ is the intrinsic partial molar isentropic compressibility of solute (disaccharide). Because it is assumed⁴³ that $K^{\circ}(\text{int}) \approx 0$, then $K_{s,2}^{\circ}(\text{elect})$ becomes equal to the partial molar isentropic compressibility at infinite dilution, $K_{s,2}^{\circ}$. The N_w values (Table 6) for Cel decrease with temperature and

Table 6. Hydration Numbers, N_w , of Disaccharides in Water and in Aqueous Solutions of BDMAAc at Temperatures $T = (288.15 \text{ to } 318.15) \text{ K}$ at 0.1 MPa

m_B mol·kg ⁻¹	N_w			
	288.15 K	298.15 K	308.15 K	318.15 K
D-(+)-Cellobiose				
0.00	4.07	3.18	2.51	2.02
0.05	3.06	1.84	1.01	0.33
0.10	3.51	2.36	1.48	0.62
0.15	3.78	2.62	1.83	1.25
0.20	3.96	2.82	2.07	1.47
D-(+)-Maltose Monohydrate				
0.00	3.38	3.09	2.40	2.06
0.05	3.44	3.10	2.40	2.06
0.10	2.32	1.74	0.77	0.31
0.15	2.66	2.13	1.24	0.68
0.20	3.11	2.63	1.75	1.33

increase with cosolute concentration from (0.05 to 0.20) mol·kg⁻¹, and in case of Mal, an increase in N_w values has been observed from (0.10 to 0.20) mol·kg⁻¹. Overall, N_w values of studied disaccharides in aqueous solutions of BDMAAc are lower than that of their magnitude in water, which suggest the existence of competing interactions between disaccharides and BDMAAc. Similar observations in N_w values have also been reported for the ternary system (sucrose + water + 3-HPAAc).¹⁹

Various microscopic and macroscopic studies of solute-water interactions were conducted^{45–48} to understand the mechanism of sweet taste chemoreception. Apparent specific volume, ASV (v_ϕ), and apparent specific isentropic compressibility, ASIC ($K_{2(s)}$), have been used extensively^{46–48} to understand taste behavior. ASV and ASIC, being the broad determinants of taste

quality of a solute in aqueous solutions, have been divided into four basic tastes:⁴⁸ salty, sweet, sour, and bitter. The values of ASVs and ASICs for the presently studied system have been calculated using the equations

$$v_\phi = V_{2,\phi}/M \quad (9)$$

$$K_{2(s)} = K_{s,2,\phi}/M \quad (10)$$

The ASV and ASIC values for Mal and Cel in water fall in the sweet taste range [$(v_\phi = (0.52 \text{ to } 0.71) \text{ cm}^3 \cdot \text{g}^{-1}, K_{2(s)} = (-3.383 \times 10^{-7} \text{ to } -2.335) \times 10^{-5} \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{bar}^{-1})$]. Furthermore, in the presence of BDMAAc, ASV and ASIC values of Mal and Cel (data not given) also fall in sweet taste range,⁴⁸ which indicates that BDMAAc does not affect the basic taste quality of the studied disaccharides. Recently, the effect of electrolytes and ionic liquids on the basic taste quality of saccharides has been reported.^{19,22,39,49} Ammonium-based protic ionic liquids^{19,22} containing an aliphatic cationic moiety (3-HPAF and 3-HPAAc) do not affect the taste quality of monosaccharides [D-(+)-glucose and D-(+)-ribose] or disaccharide (sucrose). Similarly, in the present study, the ammonium-based PIL having an aromatic cationic moiety does not affect the basic taste quality of disaccharides.

Volumetric and compressibility interaction coefficients were calculated from corresponding volume of transfer ($\Delta_t V_2^\circ$ or $\Delta_t K_{s,2}^\circ$) based on the McMillan–Mayer theory⁵⁰ of solutions using the following expression

$$\Delta_t V_2^\circ = 2Y_{AB}m_B + 3Y_{ABB}m_B^2 \quad (11)$$

where A and B denote solute (Mal or Cel) and cosolute (BDMAAc), respectively, Y_{AB} (V_{AB} or K_{AB}) represents a pair of volumetric interaction coefficients, and Y_{ABB} (V_{ABB} or K_{ABB}) represents triplet volumetric interaction coefficients (Tables 7

Table 7. Pair, V_{AB} , and Triplet, V_{ABB} , Volumetric Interaction Coefficients of Disaccharides in Aqueous Solutions of BDMAAc at $T = (288.15 \text{ to } 318.15) \text{ K}$ at 0.1 MPa

T K	$V_{AB} \cdot 10^6$ m ³ ·mol ⁻² ·kg	$V_{ABB} \cdot 10^6$ m ³ ·mol ⁻³ ·kg ²
D-(+)-Cellobiose		
288.15	15.97	−60.67
298.15	20.46	−74.90
308.15	27.65	−96.17
318.15	33.25	−114.15
D-(+)-Maltose Monohydrate		
288.15	15.96	−55.12
298.15	20.39	−69.05
308.15	28.39	−94.58
318.15	32.19	−105.89

and 8). The relative weight of the interaction coefficients (V_{AB} and V_{ABB}) may be judged from contributions to $\Delta_t V_2^\circ$ values at various molalities of the cosolute. The contributions of V_{AB} interaction coefficients for Mal and Cel are generally positive and increase linearly, whereas the triplet, V_{ABB} coefficients are negative and their magnitude increases nonlinearly (Figure 4). Furthermore, positive values of pair volumetric interaction coefficients (V_{AB} or K_{AB}) increase with temperature, whereas those of triplet interaction coefficients decrease. Triplet volumetric interaction coefficients are small, which indicate that the interactions between disaccharides and BDMAAc are mainly pair wise. Furthermore, positive values of V_{AB} and K_{AB}

Table 8. Pair, K_{AB} , and Triplet, K_{ABB} , Compressibility Interaction Coefficients of Disaccharides in Aqueous Solutions of BDMAAc at $T = (288.15 \text{ to } 318.15) \text{ K}$ at 0.1 MPa

T K	K_{AB} $\text{m}^3 \cdot \text{mol}^{-2} \cdot \text{Pa}^{-1} \cdot \text{kg}$	K_{ABB} $\text{m}^3 \cdot \text{mol}^{-3} \cdot \text{Pa}^{-1} \cdot \text{kg}^2$
D-(+)-Cellobiose		
288.15	65.73	−211.83
298.15	81.12	−255.96
308.15	92.44	−292.04
318.15	110.91	−350.24
D-(+)-Maltose Monohydrate		
288.15	74.88	−232.45
298.15	87.56	−270.09
308.15	100.65	−306.00
318.15	113.00	−343.27

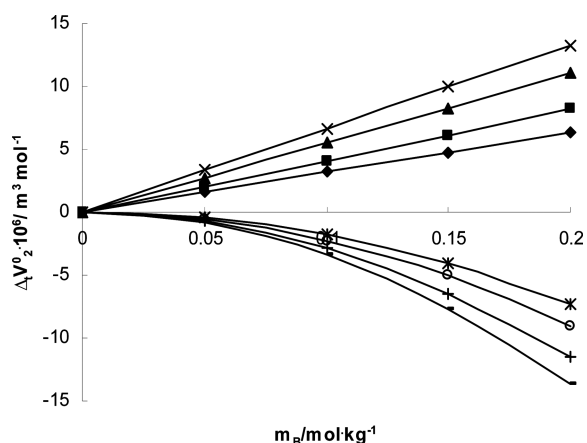


Figure 4. Contributions of volumetric interaction coefficients to $\Delta_i V_2^\circ$ of Cel at various molalities of BDMAAc: \blacklozenge and \times , 288.15; \blacksquare and \circ , 298.15; \blacktriangle and $+$, 308.15; and \times and $-$, 318.15 K [$\blacklozenge, \blacksquare, \blacktriangle$, and \times for V_{AB} and $\circ, +$, and $-$ for V_{ABB}].

parameters suggest that interactions occur due to the overlap of hydration cospheres of disaccharides and ions of BDMAAc.

4. CONCLUSIONS

Volumetric properties of D-(+)-maltose monohydrate and D-(+)-cellobiose in water and in aqueous solutions of BDMAAc were studied at temperatures $T = (288.15 \text{ to } 318.15) \text{ K}$ and at atmospheric pressure from precise density, ρ , and speed of sound, u , measurements. The V_2° values of Mal and Cel in aqueous BDMAAc solutions increase up to $\approx 0.05 \text{ mol} \cdot \text{kg}^{-1}$; thereafter, V_2° values decrease with PIL concentration, and a similar trend has also been observed for $K_{s,2}^\circ$ values. The compressibility transfer parameter, $\Delta_i K_{s,2}^\circ$, was found to be positive for both disaccharides, whereas both positive and negative magnitudes of $\Delta_i V_2^\circ$ values were observed only in the case of Cel. The $\Delta_i V_2^\circ$ and $\Delta_i K_{s,2}^\circ$ values first increase with concentration of BDMAAc up to $\approx 0.05 \text{ mol} \cdot \text{kg}^{-1}$; afterwards, the values start decreasing at all studied temperatures, indicating the presence of competing interactions between disaccharides and BDMAAc.

The taste quality of Mal and Cel in water and in aqueous solutions of BDMAAc has also been studied on the basis of the range covered by ASV and ASIC parameters. Both ASV and ASIC values for Mal and Cel in water and in aqueous BDMAAc

solutions fall in to the sweet taste range, which suggests that the taste quality of disaccharides is not affected by PILs.

■ ASSOCIATED CONTENT

Supporting Information

Second derivative, $(\partial^2 V_2^\circ / \partial T^2)_P$, values of disaccharides in water and in aqueous BDMAAc solutions. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/je501169y.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tsbanipal@yahoo.com. Phone: +91 183 2451357. Fax: +91 183 2258819/20.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

V.S. is grateful to UGC-New Delhi, India, for providing financial support under the program of the Dr. D. S. Kothari postdoctoral fellowship (DSKPDF). The authors are also grateful to Mr. D. Keshapolla for the synthesis and characterization of BDMAAc.

■ REFERENCES

- (1) Freire, M. G.; Claudio, A. F. M.; Araujo, J. M. M.; Coutinho, J. A. P.; Marrucho, I. M.; Lopes, J. N. C.; Rebelo, L. P. N. Aqueous Biphasic Systems: A Boost Brought About by Using Ionic Liquids. *Chem. Soc. Rev.* **2012**, *41*, 4966–4995.
- (2) Mejia, I.; Stanley, K.; Canales, R.; Brennecke, J. F. On the High-Pressure Solubilities of Carbon Dioxide in Several Ionic Liquids. *J. Chem. Eng. Data* **2013**, *58*, 2642–2653.
- (3) Shekari, H.; Kazempour, A. Solution Properties of Ternary D-Glucose+1-Ethyl-3-methylimidazolium Ethyl Sulfate+Water Solutions at 298.15 K. *J. Sol. Chem.* **2011**, *40*, 1582–1595.
- (4) Fauzi, A. H. M.; Amin, N. A. S. An Overview of Ionic Liquids as Solvents In Biodiesel Synthesis. *Renew. Sust. Energy Rev.* **2012**, *16*, 5770–5786.
- (5) Hassan, E. S. R. E.; Mutelet, F.; Pontvianne, S.; Moise, J. C. Studies on the Dissolution of Glucose in Ionic Liquids and Extraction Using the Antisolvent Method. *Environ. Sci. Technol.* **2013**, *47*, 2809–2816.
- (6) Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. Thermophysical Properties of Imidazolium-Based Ionic Liquids. *J. Chem. Eng. Data* **2004**, *49*, 954–964.
- (7) Plechkova, N. V.; Seddon, K. R. Applications of Ionic Liquids in the Chemical Industry. *Chem. Soc. Rev.* **2008**, *37*, 123–150.
- (8) Murugesana, S.; Linhardt, R. J. Ionic Liquids in Carbohydrate Chemistry-Current Trends and Future Directions. *Curr. Org. Syn.* **2005**, *2*, 437–451.
- (9) Swatoski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. Dissolution of Cellulose with Ionic Liquids. *J. Am. Chem. Soc.* **2002**, *124*, 4974–4975.
- (10) Xu, A.; Zhang, Y.; Zhao, Y.; Wang, J. Cellulose Dissolution at Ambient Temperature: Role of Preferential Solvation of Cations of Ionic Liquids By a Cosolvent. *Carbohydr. Polym.* **2013**, *92*, 540–544.
- (11) Fischer, S.; Leipner, H.; Thummler, K.; Brendler, E.; Peters, J. Inorganic Molten Salts as Solvents For Cellulose. *Cellulose* **2003**, *10*, 227–236.
- (12) Pinkert, A.; Marsh, K. N.; Pang, S.; Staiger, M. P. Ionic Liquids and Their Interaction with Cellulose. *Chem. Rev.* **2009**, *109*, 6712–6728.
- (13) Zakrzewska, M. E.; Lukasik, E. B.; Lukasik, R. B. Ionic Liquid-Mediated Formation of 5-Hydroxymethylfurfurals a Promising Biomass-Derived Building Block. *Chem. Rev.* **2011**, *111*, 397–417.

- (14) Youngs, T. G. A.; Holbrey, J. D.; Mullan, C. L.; Norman, S. E.; Lagunas, M. C.; D'Agostino, C.; Mantle, M. D.; Gladden, L. F.; Bowron, D. T.; Hardacre, C. Neutron Diffraction, NMR and Molecular Dynamics Study of Glucose Dissolved in the Ionic Liquid 1-Ethyl-3-methylimidazolium Acetate. *Chem. Sci.* **2011**, *2*, 1594–1605.
- (15) Jin, H. X.; Chen, H. Y. Volumetric Properties of 1-Butyl-3-methylimidazolium Tetrafluoroborate-Glucose-Water Systems. *J. Chem. Eng. Data* **2012**, *57*, 1134–1138.
- (16) Jin, H. X.; Chen, H. Y. Volumetric Properties for Ionic Liquid-Sucrose-Water Systems. *J. Chem. Eng. Data* **2011**, *56*, 4392–4395.
- (17) Shekaari, H.; Kazempour, A. Density and Viscosity in Ternary D-Xylose + Ionic Liquid (1-Alkyl-3-methylimidazolium Bromide) + Water Solutions at 298.15 K. *J. Chem. Eng. Data* **2012**, *57*, 3315–3320.
- (18) Zhuo, K.; Chen, Y.; Chen, J.; Bai, G.; Wang, J. Interactions of 1-Butyl-3-Methylimidazolium Carboxylate Ionic Liquids with Glucose in Water: A Study of Volumetric Properties, Viscosity, Conductivity and NMR. *Phys. Chem. Chem. Phys.* **2011**, *13*, 14542–14549.
- (19) Singh, V.; Chhotaray, P. K.; Gardas, R. L. Effect of Protic Ionic Liquid on the Volumetric Properties and Taste Behaviour of Sucrose. *Food Chem.* **2015**, *169*, 478–483.
- (20) Shekaari, H.; Kazempour, A. Dehydration Effect of Ionic Liquid, 1-Pentyl-3-methylimidazolium Bromide, on the Aqueous D-glucose Solutions: Thermodynamic Study. *J. Taiwan Inst. Chem. Eng.* **2012**, *43*, 650–657.
- (21) Wu, B.; Zhang, Y. M.; Wang, H. P. Volumetric Properties and Conductivities of 1-Butyl-3-methylimidazolium Tetrafluoroborate + Sucrose + Water Mixtures. *J. Chem. Eng. Data* **2009**, *54*, 1430–1434.
- (22) Singh, V.; Chhotaray, P. K.; Gardas, R. L. Solvation Behaviour and Partial Molar Properties of Monosaccharides in Aqueous Protic Ionic Liquid Solutions. *J. Chem. Thermodyn.* **2014**, *71*, 37–49.
- (23) Payal, R. S.; Balasubramanian, S. Dissolution of Cellulose in Ionic Liquids: An Ab Initio Molecular Dynamics Simulation Study. *Phys. Chem. Chem. Phys.* **2014**, *16*, 17458–17465.
- (24) Payal, R. S.; Bharath, R.; Periyasamy, G.; Balasubramanian, S. Density Functional Theory Investigations on the Structure and Dissolution Mechanisms for Cellobiose and Xylan in an Ionic Liquid: Gas Phase and Cluster Calculations. *J. Phys. Chem. B* **2012**, *116*, 833–840.
- (25) Zhang, J.; Zhang, H.; Wu, J.; Zhang, J.; Hea, J.; Xiang, J. NMR Spectroscopic Studies of Cellobiose Solvation in EmimAc Aimed to Understand the Dissolution Mechanism of Cellulose in Ionic Liquids. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1941–1947.
- (26) Choi, H. M.; Kwon, I. Dissolution of Zein Using Protic Ionic Liquids: N-(2-Hydroxyethyl) Ammonium Formate and N-(2-Hydroxyethyl) Ammonium Acetate. *Ind. Eng. Chem. Res.* **2011**, *50*, 2452–2454.
- (27) Melo, C. I.; Bogel-Lukasik, R.; da Ponte, M. N.; Bogel-Lukasik, E. Ammonium Ionic Liquids as Green Solvents for Drugs. *Fluid Phase Equilib.* **2013**, *338*, 209–216.
- (28) Almeida, H. F. D.; Passos, H.; Lopes-da-Silva, J. A.; Fernandes, A. M.; Freire, M. G.; Coutinho, J. A. P. Thermophysical Properties of Five Acetate-Based Ionic Liquids. *J. Chem. Eng. Data* **2012**, *57*, 3005–3013.
- (29) Keshapolla, D.; Singh, V.; Gardas, R. L. Volumetric, Acoustic and Transport Properties of Binary Mixtures of Benzyltrimethylammonium Based Ionic Liquids with N,N-Dimethylformamide at Temperature from 293.15 to 328.15 K. *J. Mol. Liq.* **2014**, *199*, 330–338.
- (30) Anouti, M.; Caravanier, M. C.; Floch, C. L.; Lemordant, D. Alkylammonium-Based Protic Ionic Liquids Part I: Preparation and Physicochemical Characterization. *J. Phys. Chem. B* **2008**, *112*, 9406–9411.
- (31) Kell, G. S. Density, Thermal Expansivity and Compressibility of Liquid Water From 0° to 150° C. Correlations and Tables for Atmospheric Pressure and Saturation Reviewed and Expressed on 1968 Temperature Scale. *J. Chem. Eng. Data* **1975**, *20*, 97–105.
- (32) Chirico, R. D.; Frenkel, M.; Magee, J. W.; Diky, V.; Muzny, C. D.; Kazakov, A. F.; Kroenlein, K.; Abdulgatov, I.; Hardin, G. R.; Acree, W. A.; Brenneke, J. F.; Brown, P. L.; Cummings, P. T.; de Loos, T. W.; Friend, D. G.; Goodwin, A. R. H.; Hansen, L. D.; Haynes, W. M.; Koga, N.; Mandelis, A.; Marsh, K. N.; Mathais, P. M.; McCabe, C.; O'Connell, J. P.; Padua, A.; Rives, V.; Schick, C.; Trusler, J. P. M.; Vyazovkin, S.; Weir, R. D.; Wu, J. Improvement of Quality in Publication of Experimental Thermophysical Property Data: Challenges, Assessment Tools, Global Implementation, and Online Support. *J. Chem. Eng. Data* **2013**, *58*, 2699–2716.
- (33) Kikuchi, M.; Sakurai, M.; Nitta, K. Partial Molar Volumes and Isentropic Compressibilities of N-Acetyl Amino Acid Amides in Dilute Aqueous Solutions at (5, 15, 25, 35, and 45) °C. *J. Chem. Eng. Data* **1996**, *41*, 1439–1445.
- (34) Banipal, P. K.; Singh, V.; Banipal, T. S. Effect of Sodium Acetate on the Volumetric Behaviour of Some Mono-, Di-, And Tri-Saccharides in Aqueous Solutions over Temperature Range (288.15 to 318.15) K. *J. Chem. Thermodyn.* **2010**, *42*, 90–103.
- (35) Banipal, P. K.; Chahal, A. K.; Banipal, T. S. Studies on Volumetric Properties of Some Saccharides in Aqueous Potassium Chloride Solutions over Temperature Range (288.15 to 318.15) K. *J. Chem. Thermodyn.* **2009**, *41*, 452–483.
- (36) Banipal, P. K.; Singh, V.; Kaur, G.; Kaur, M.; Banipal, T. S. Thermodynamic and Transport Properties of Some Disaccharides in Aqueous Ammonium Sulfate Solutions at Various Temperatures. *J. Chem. Eng. Data* **2008**, *53*, 1713–1724.
- (37) Banipal, P. K.; Aggarwal, N.; Banipal, T. S. Study on Interactions of Saccharides and Their Derivatives with Potassium Phosphate Monobasic (1:1 Electrolyte) in Aqueous Solutions at Different Temperatures. *J. Mol. Liq.* **2014**, *196*, 291–299.
- (38) Herrington, T. M.; Pethybridge, A. D.; Parkin, B. A.; Roffey, M. G. Apparent Molar Volumes of Aqueous Cellobiose Solutions. *J. Chem. Soc., Faraday Trans. I* **1983**, *79*, 845–852.
- (39) Banipal, P. K.; Singh, V.; Banipal, T. S.; Singh, H. Ultrasonic Studies of Some Mono-, Di-, and Tri-Saccharides in Aqueous Sodium Acetate Solutions at Different Temperatures. *Z. Phys. Chem.* **2013**, *227*, 1707–1722.
- (40) Galema, S. A.; Hoiland, H. Stereochemical Aspects of Hydration of Carbohydrates in Aqueous Solutions. 3. Density and Ultrasound Measurements. *J. Phys. Chem.* **1991**, *95*, 5321–5326.
- (41) Kirkwood, J. G. Theoretical Studies upon Dipolar Ions. *Chem. Rev.* **1939**, *24*, 233–251.
- (42) Ramasami, P.; Kakkar, R. Partial Molar Volumes and Adiabatic Compressibilities at Infinite Dilution of Aminocarboxylic Acids and Glycylglycine in Water and Aqueous Solutions of Sodium Sulphate at (288.15, 298.15 and 308.15) K. *J. Chem. Thermodyn.* **2006**, *38*, 1385–1395.
- (43) Millero, F. J.; Antonio, L. S.; Charles, S. The Apparent Molal Volumes and Adiabatic Compressibilities of Aqueous Amino Acids at 25 °C. *J. Phys. Chem.* **1978**, *82*, 784–792.
- (44) Millero, F. J.; Ward, G. K.; Lepple, F. K.; Hoff, E. V. Isothermal Compressibility of Aqueous Sodium Chloride, Magnesium Chloride, Sodium Sulfate, and Magnesium Sulfate Solutions from 0 to 45° at 1 Atm. *J. Phys. Chem.* **1974**, *16*, 1636–1643.
- (45) Birch, G. G. Role of Water in Sweet Taste Chemoreception. *Pure Appl. Chem.* **2002**, *74*, 1103–1108.
- (46) Birch, G. G.; Parke, S.; Siertsema, R.; Westwell, J. M. Specific Volumes and Sweet Taste. *Food Chem.* **1996**, *56*, 223–230.
- (47) Mathlouthi, M.; Hutteau, F.; Angibous, J. F. Physicochemical Properties and Vibrational Spectra of Small Carbohydrates in Aqueous Solution and the Role of Water in Their Sweet Taste. *Food Chem.* **1996**, *56*, 215–221.
- (48) Parke, S. A.; Birch, G. G.; Dijk, R. Some Taste Molecules and Their Solution Properties. *Chem. Senses* **1999**, *24*, 271–279.
- (49) Banipal, P. K.; Singh, V.; Aggarwal, N.; Banipal, T. S. Hydration Behaviour of Some Mono-, Di-, and Tri-saccharides in Aqueous Sodium Gluconate Solutions at (288.15, 298.15, 308.15 and 318.15) K: Volumetric and Rheological Approach. *Food Chem.* **2015**, *168*, 142–150.
- (50) McMillan, W. G., Jr.; Mayer, J. E. The Statistical Thermodynamics of Multicomponent Systems. *J. Chem. Phys.* **1945**, *13*, 276–305.