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Density study of (D (+) mannose + water), (D (+) mannose + water + sodium cyclamate), (D (+) maltose monohydrate + water) and (D (+) maltose monohydrate + water + sodium cyclamate) systems at T = 298.15 K

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ABSTRACT

Effect of different concentrations of aqueous solutions of sodium cyclamate on sugars (mono and disaccharides) are observed by measuring the densities of (sugar + water) and (sugar + water + sodium cyclamate) systems. Densities of aqueous solutions of D(+) mannose (monosaccharide) and D(+) maltose monohydrate (disaccharide) in (0.05, 0.15, 0.3) mol.kg^{-1} of sodium cyclamate (Na-Cyclamate) at T = 298.15 K have been measured. From experimental values of densities, $V\phi^0$ (partial molar volumes) $\Delta_{trs}V\phi^0$ (partial molar volumes of transfer) ASV (apparent specific volumes) interaction parameters (V_{AB}) and (V_{ABB}) have been determined. The calculated values of various parameters have been used to interpret the results in terms of (D (+) mannose–water), (D(+) mannose–water–Na-cyclamate), (D(+) maltose monohydrate–water) and (D(+) maltose monohydrate –water–Na-cyclamate) interactions in sugar–water–Na-cyclamate and quality of taste sense of solutions.

Keywords: Density, D(+) mannose, D(+) maltose monohydrate, Apparent specific volume.

INTRODUCTION

Carbohydrate gain importance and attention of researchers because of their multifunctional and significant roles in different areas like biological reaction, industrial field, pharmaceuticals, organic synthesis, structural determination and separation. The stabilities of such compounds and their position are verbalized by thermodynamic consideration[1]. Sugars are the energetic biomolecule of living being. Sugar solutions are of considerable interest in various aspects of basic researches and application. Interactions of sugars with sweetener in aqueous media and its hydration properties are of significant biological and thermodynamic importance. Combinations of Non-caloric sweetener are mostly used to formulate pharmaceutical doses and food products.

Combination of two sweeteners results in synergistic effect which means sweetness of mixture or combination is high as compare with the sweetness of individual sugar. This was reported true in some blends of such sweetener[2]. Also by combining with other sugars reduces the bitterness of one of the sugar and enhances the taste quality. Application of non-nutritive sugars or artificial sugars are less caloric and thus provides choices for caloric sugars, reduces weight, assistance in the management of diabetes, provides cost effectiveness[3], also have many applications in food and pharmaceutical industry.

For present work one monosaccharide (D(+) mannose) and one disaccharide (D(+) maltose monohydrate) taken. Mannose is a monosaccharide consists of one sugar unit and belongs to aldohexoses. It is nutritional and healthy food supplement. It is a natural bioactive. Maltose monohydrate also known as malt sugar, compose of two glucose unit join to each other by α 1-4-glycosidic bond. It plays important role in energy metabolism.

This paper reports densities of D(+) mannose–water, D(+) mannose–water–Na-cyclamate, D(+) maltose monohydrate–water, and D(+) maltose monohydrate–water–Na-cyclamate systems at 298.15 K. Furthermore, the parameter calculated from densities of aqueous solutions are reported to obtain the information regarding interactions present in D(+) mannose–water, D(+) mannose–water– Na-cyclamate, D(+) maltose monohydrate–water, and D(+) maltose monohydrate–water–Na-cyclamate systems.

MATERIAL AND METHODS

D(+) Mannose, D(+) Maltose monohydrate and Sodium cyclamate were bought from suppliers Sigma Aldrich used for this study. Table 1. includes the details of chemicals.

Table 1: Chemicals details

Chemical name	CAS Number	Molar mass	%Purity
D(+) Mannose	M8574	180.36	≥ 99.0%
D(+) Maltose monohydrate	M5885	360.31	≥ 99.0%
Sodium Cyclamate	71440	201.22	≥ 99.0%

Aqueous solutions of D(+) mannose and D(+) maltose monohydrate were freshly prepared using triply distilled water. In dry airtight stoppered glass bottle solutions were prepared using weight/ weight method. Dhona balance accurate to 0.0001 g was used to undertake weight of solute and solvent. Densities were measured in glass-walled thermostat at 298.15 K using Bi-capillary pycnometer[4-7] with bulb sizeof 15cm^3 volume. Triply distilled water and pure organic solvents were used to calibrate pycnometer. Observed uncertainties in temperature and measured density were 0.005 K and 5.4 ×10^{-2} kg m^{-3}, respectively.

RESULT AND DISSCUSION

In this present work, aqueous solutions of sugars (D(+) mannose and D(+) maltose monohydrate) in (0.05, 0.15, 0.3) mol.kg^{-1} of Na-Cyclamate have been studied at T = 298.15 K. Density data of sugars (mono and disaccharides) of concentration ranges from (0.04 to 0.2) mol. kg^{-1} in water and in (0.05, 0.15, 0.3) mol.kg^{-1} Na-Cyclamate at T = 298.15 K have been generated. From the experimentally measured density values, apparent molar volume (V_ϕ) values are calculated using equation no.1.[8-9].

$$V_\phi = \frac{M}{\rho} - \frac{\rho - \rho_0}{m\rho\rho_0} \quad (1)$$

Where, M is molar mass of the solute, and m molality of the solution, ρ_o density of solvent, and ρ density of the aqueous solution. Literature[10] value for density of water (ρ_o = 997.07 kg.m^{-3}) at T = 298.15 K has been considered for the calculation of V_ϕ. Calculated values of (ρ) and (V_ϕ) for aqueous solutions of (D(+) mannose and D(+) maltose monohydrate) in (0.05, 0.15, 0.3) mol.kg^{-1} of Na-Cyclamate are given in Table 2 and 3.

From the measured density data, it is understood that density of solutions of (D(+) mannose and D(+) maltose monohydrate) in water and in Na-Cyclamate varies linearly with molalities.

Fig. 1 and Fig. 2 show 3-D plots of (V_ϕ) vs (m) of (D(+) mannose and D(+) maltose monohydrate) in (water) and in (0.05, 0.15, 0.3) mol. kg^{-1} of Na-Cyclamate, respectively at T = 298.15K.

Table 2: Density (ρ) and apparent molar volume (V_ϕ) values of D(+) mannose in water and (0.05, 0.15, 0.3) mol.kg^{-1} of Na-Cyclamate at T = 298.15 K

m (mol.kg^{-1})	ρ (kg.m^{-3})	$10^6 V_\phi$ (m^3.mol^{-1})	m (mol.kg^{-1})	ρ/(kg.m^{-3})	$10^6 V_\phi$ (m^3.mol^{-1})
D(+) mannose + Water			D(+) mannose + (0.05) m Na-cyclamate		
0.0402	999.81	111.99	0.0403	1003.82	112.31
0.0803	1002.48	112.31	0.0806	1006.50	112.51
0.1203	1005.11	112.56	0.1196	1009.05	112.74
0.1604	1007.70	112.82	0.1602	1011.66	113.00
0.2005	1010.24	113.12	0.1990	1014.11	113.26
D(+) mannose + (0.15) *m* Na-cyclamate			D(+) mannose + (0.3) *m* Na-cyclamate		
0.0402	1011.11	112.55	0.0401	1022.74	112.81
0.0803	1013.75	112.79	0.0800	1025.33	113.16
0.1197	1016.30	113.04	0.1200	1027.89	113.44
0.1604	1018.89	113.29	0.1603	1030.40	113.69
0.1998	1021.35	113.56	0.2000	1032.84	113.95

Table 3: Density (ρ) and apparent molar volume (V_ϕ) values of D(+) maltose monohydrate in water and (0.05, 0.15, 0.3) mol.kg^{-1} of Na-Cyclamate at T = 298.15 K

m (mol.kg^{-1})	(kg.m^{-3})	$10^6 V_\phi$ (m^3.mol^{-1})	m (mol.kg^{-1})	ρ/(kg.m^{-3})	$10^6 V_\phi$ (m^3.mol^{-1})
D (+) maltose monohydrate + Water			D (+) maltose monohydrate + (0.05) m Na-cyclamate		
0.0400	1002.31	228.34	0.0401	1006.32	228.83
0.0801	1007.44	228.76	0.0801	1011.41	229.12
0.1199	1012.42	229.07	0.1202	1016.39	229.48
0.1599	1017.31	229.39	0.1600	1021.22	229.82
0.1999	1022.10	229.65	0.1999	1025.96	230.06
D (+) maltose monohydrate + (0.05) m Na-cyclamate			D (+) maltose monohydrate + (0.05) m Na-cyclamate		
0.0399	1013.57	229.21	0.0400	1024.59	229.43
0.0800	1018.63	229.48	0.0801	1029.59	229.74
0.1199	1023.55	229.76	0.1201	1034.46	229.96
0.1601	1028.39	230.09	0.1601	1039.22	230.27
0.2002	1033.11	230.39	0.2000	1043.88	230.48

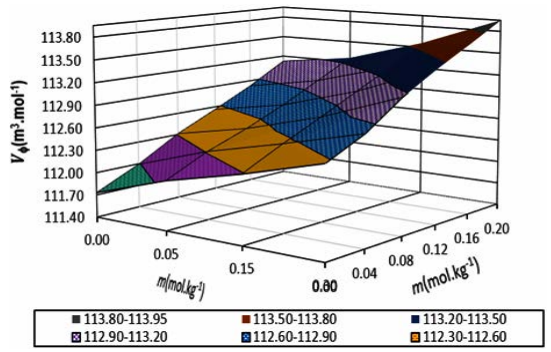

Fig. 1. 3-D Plots of (V_ϕ) vs (m) of (D(+) mannose in (water) and in (0.05, 0.15, 0.3) mol.kg^{-1} of Na-Cyclamate at T = 298.15 K

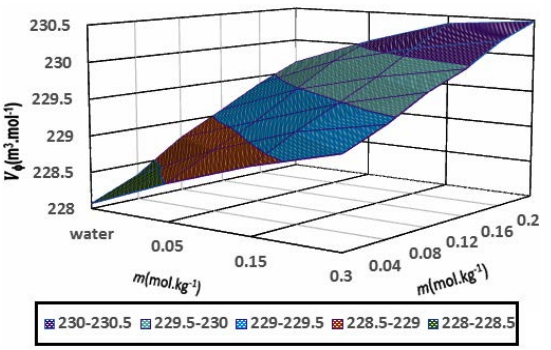

Fig. 2. 3-D Plots of (V_ϕ) vs (m) of (D(+) maltose monohydrate in (water) and in (0.05, 0.15, 0.3) mol.kg^{-1} of Na-Cyclamate at T = 298.15 K

Figure 1 and Figure 2 show the effect of concentration of Na-cyclamate on the V_ϕ values for D(+) mannose and D(+) maltose monohydrate. V_ϕ varies linearly with the concentration of (D(+) mannose and D(+) maltose monohydrate) in water and in (0.05, 0.15, 0.3) mol.kg^{-1} of Na-Cyclamate at T = 298.15 K. V_ϕ of (D(+) mannose and D(+) maltose monohydrate) increases with increase in molality of Na-cyclamate.

Equation 2 shows the correlation between calculated V_ϕ and m[11].

$$V_\phi = V_\phi^0 + S_v.m \quad (2)$$

Where V_ϕ^0 is the partial molar volume, V_ϕ *m* and S_v are apparent molar volume, (solute-solute) interaction parameter, and m molality, respectively. V_ϕ^0 and V_ϕ were calculated using least square method. The V_ϕ^0 values throw light on valuable information about strength of the solute-solvent interactions[12-13]. Table 4 and 5 summarise the values of V_ϕ^0 and S_v .

Table 4: V_ϕ^0, S_v, ASV, $\Delta_{trs} V_\phi^0$ of D(+) mannose in water and (0.05, 0.15, 0.3) mol.kg^{-1} Na-cyclamate at *T* = 298.15 K

	Water	0.05 *m*	0.15 *m*	0.3 *m*
10^6 V_ϕ^0	111.73	112.05	112.29	112.57
10^6 S_v	6.918	5.965	6.289	7.013
10^6 ASV	0.62	0.622	0.623	0.625
10^6 $\Delta_{trs} V_\phi^0$	-	0.32	0.56	0.84

Table 5: V_ϕ^0, S_v, ASV, $\Delta_{trs} V_\phi^0$ of D(+) maltose monohydrate in water and (0.05, 0.15, 0.3) mol.kg^{-1} Na-cyclamate at *T* = 298.15 K

	Water	0.05 *m*	0.15 *m*	0.3 *m*
10^6 V_ϕ^0	228.07	228.51	228.89	229.19
10^6 S_v	8.133	7.91	7.423	6.572
10^6 ASV	0.633	0.634	0.635	0.636
10^6 $\Delta_{trs} V_\phi^0$	-	0.44	0.82	1.12

It is observed that with increasing concentration of solute and cosolute, V_ϕ^0 values go on increasing. This observed behaviour of V_ϕ^0 is due to the strong [(D(+) mannose and D(+) maltose monohydrate)–cosolute (Na-cyclamate)] interactions. Reported and experimental V_ϕ^0 values for D(+) mannose and D(+) maltose monohydrate in water at *T* = 298.15 K were compared. The reported V_ϕ^0 values for D(+) mannose in water are (111.72[14], 111.70[15], 111.70[23]) × 10^{-6} $m^3.mol^{-1}$ at *T* = 298.15 K while experimental V_ϕ^0 value is 111.73 × 10^{-6} $m^3.mol^{-1}$ at *T* = 298.15 K. The reported values of V_ϕ^0 D (+) maltose monohydrate in water are (228.12[15], 228.14[16], 227.78[17]) × 10^{-6} $m^3.mol^{-1}$ at 298.15 K and experimental V_ϕ^0 value is 228.07 × 10^{-6} $m^3.mol^{-1}$ at *T* = 298.15 K. The reported V_ϕ^0 values and experimental V_ϕ^0 values for studied mono and disaccharides are very close. Experimentally observed S_v values are positive and smaller than V_ϕ^0 values interprets strong solute–solvent interaction than solute–solute interaction.

The values of standard transfer partial volume ($\Delta_{trs} V_\phi^0$) are estimated to focus on the nature and extent of solute–cosolute interactions. $\Delta_{trs} V^0$ at infinite dilution of sugar solutions from water to Na-cyclamate have been calculated using Equation (3).

$$\Delta_{trs} V_\phi^0 = V_\phi^0 \text{ (in aqueous sodium cyclamate)} - V_\phi^0 \text{ (in water)} \quad (3)$$

$\Delta_{trs} V_\phi^0$ values for (D(+) mannose and D(+) maltose monohydrate in (0.05, 0.15, 0.3) mol.kg^{-1} of Na-Cyclamate at *T* = 298.15 K are reported in Table 4 and Table 5, respectively. Positive $\Delta_{trs} V_\phi^0$ values are observed for (D(+) mannose and D(+) maltose monohydrate) in water and in presence of Na- cyclamate. $\Delta_{trs} V_\phi^0$ values go on increasing with increase in concentration of Na-cyclamate. Dey P. C *et al.,*[18] show the same trend in results, Banipal *et al.,*[19] reported $\Delta_{trs} V_\phi^0$ values for all D(+) mannose and D(+) maltose monohydrate) studied as positive and increase with increase in concentration of guanidine hydrochloride. Authors[20] also reported same trend in results for $\Delta_{trs} V_\phi^0$ values of sugars in presence of cosolute. The concentration effect of co-solute (Na-cyclamate) on $\Delta_{trs} V_\phi^0$ values of (D(+) mannose and D(+) maltose monohydrate) shown in Figure 3.

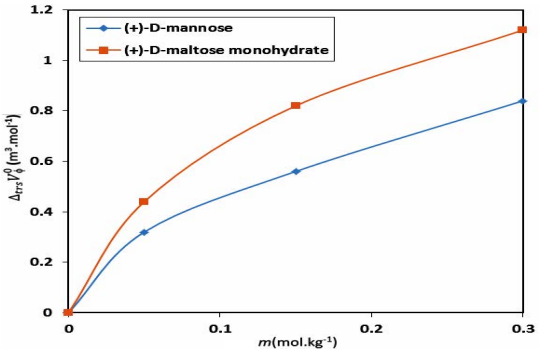

Fig. 3. Plot of standard transfer partial volume ($\Delta_{trs} V_\phi^0$) vs molality m of aqueous solution of (0.05, 0.15, 0.3) mol. kg^{-1} Na-cyclamate for D(+) mannose and D(+) maltose monohydrate at *T* = 298.15 K

From Fig. 3, we observed that $\Delta_{trs} V_\phi^0$ increases with increase in the molecular complexity from mono to disaccharides. $\Delta_{trs} V_\phi^0$ values for D(+) maltose monohydrate is high as compared with $\Delta_{trs} V_\phi^0$ values of D(+) mannose. This is due to addition of one sugar unit in disaccharide as compared to monosaccharide. Additional (-OH) group and (-O-) glycosidic bond in maltose monohydrate responsible for this effect as compared with mannose. $\Delta_{trs} V_\phi^0$ values for D(+) mannose and D(+) maltose monohydrate in presence of Na-cyclamate increase with the molality of cosolute (Na-cyclamate) suggests stronger interaction between polar groups (–C=O,

–OH and–O–) group of D(+) mannose and D(+) maltose monohydrate) and ions (Na+)/(cyclamate-) of Na-cyclamate. Prevalence of interaction between hydrophilic groups of sugars and ions of cosolute leads to dehydration of sugars.

At an infinite dilution when the V_ϕ of sugar is equal to V_ϕ^0 can be expressed using Shahidi's equation[21] as given below

$$V_\phi^0 = V_{V.W} + V_{void} - V_{shrinkage} \quad (4)$$

Where $V_{V.W}$ denotes the van der Waals volume, V_{void} represents empty volume and $V_{shrinkage}$ is the shrinkage volume due to solute-water interactions. $V_{shrinkage}$ arise due to hydrogen bonding between water molecule and hydroxyl group of sugars. The magnitude of $V_{V.W}$ and V_{void} are same in presence of water and aqueous electrolyte solutions. Thus the positive $\Delta_{trs} V_\phi^0$ is because of decrease in shrinkage volume which is further due to the reduced electrostriction of water[20] in aqueous solutions of Na- cyclamate. Thus the positive $\Delta_{trs} V_\phi^0$ values depict the sugar dehydration in aqueous solutions of Na-cyclamate.

Equation (5) has been used for calculation of interaction parameters (V_{AB} (doublet) and V_{ABB} (triplet)) using $\Delta_{trs} V_\phi^0$ based on McMillan-Mayer theory of solutions.[22-23]

$$\Delta_{trs} V_\phi^0 = 2V_{AB}m_B + 3V_{ABB} m_B^2 + \quad (5)$$

Where A symbolizes sugars (D(+) mannose and D(+) maltose monohydrate) and B symbolizes Na-cyclamate. By using least square method values of V_{AB} and V_{ABB} were calculated. The observed values of (V_{AB}) and (V_{ABB}) interaction parameters are reported in Table 6.

Table 6 : V_{AB} and V_{ABB} for D(+) mannose and D(+) maltose monohydrate at T = 298.15 K

(V_{AB})/(V_{ABB})	D(+) mannose	D(+) maltose monohydrate
$V_{AB} \times 10^6$ ($m^3 mol^{-2}$ kg)	2.634	3.921
$V_{ABB} \times 10^6$ ($m^3 mol^{-2}$ kg^2)	-2.775	-4.598

The sign of magnitude of V_{AB} and V_{ABB} values predicts which kind of interactions occurring between sugars (D(+) mannose and D(+) maltose monohydrate) and Na-cyclamate. For all studied solutions positive V_{AB} values and negative V_{ABB} values suggest pairwise interactions. The positive values of V_{AB} have been interpreted by group additivity model[24-26]. This model suggest four types of interaction occurs between the polar groups of sugars and ions of electrolyte as (Hydrophilic–ionic, hydrophobic–ionic, hydrophilic-hydrophilic interaction between polar group, and hydrophobic-hydrophobic interaction between non-polar groups).

According to structural interaction and hydration models[27-28], the positive contribution to V_{AB} is due to sugar-cation interaction. Thus positive values of V_{AB} for studied systems are contributed by interaction between polar (hydrophilic) groups of D(+) mannose and D(+) maltose monohydrate) and ions of Na- cyclamate.

The valuable information about quality of taste for studied solutions of D(+) mannose and D(+) maltose monohydrate in absence/presence of Na-cyclamate can be obtained from apparent specific volume (ASV). Values of ASV were calculated using equation

$$ASV = V_\phi^0/M \quad (6)$$

Apparent specific volume values estimate about the taste quality of sweeteners and distinguish them as sweet, salty, sour and bitter[29]. The complete variety of human taste responsiveness is more or less narrowed to ASV[30] between (0.1-0.9) $m^3 . kg^{-1}$. ASV value range from (0.51- 0.71) $\times 10^{-6}$ $m^3 . kg^{-1}$ fit nicely for sweet taste molecules reported by Shamil *et al.,*[31]. ASV value[32] for perfect sweet taste obtained at middle of the range 0.618×10^{-6} $m^3 . kg^{-1}$.

Table 4 and Table 5 report observed values of ASV for (D(+) mannose and D(+) maltose monohydrate) in water (0.05, 0.15, 0.3) mol.kg^{-1} of Na-Cyclamate at T = 298.15 K, respectively. Experimentally observed ASV values for studied systems lies in the range from (0.620-0.636) $\times 10^{-6}$ $m^3 . kg^{-1}$. Thus, studied all solutions show sweet taste. ASV values for D(+) mannose and D(+) maltose monohydrate increases with increase in concentration of Na-cyclamate. Fig. 4 shows the variations of ASV values for D(+) mannose and D(+) maltose monohydrate with molality of Na-cyclamate.

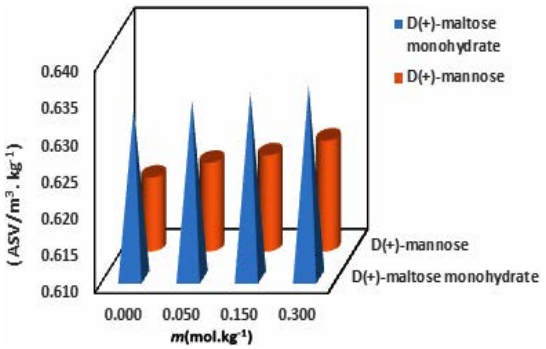

Fig. 4. Plot of ASV of D (+) mannose and D (+) maltose monohydrate vs *m* of Na-cyclamate at T = 298.15 K

CONCLUSION

From measured density values volumetric parameters V_ϕ^0, S_v, ASV, $\Delta_{trs}\ V_\phi^0$ and interaction parameters (V_{AB} and V_{ABB}) have been calculated. The observed values reveal the following conclusions.

1. Observed positive values of V_ϕ^0 specify strong sugar-water interactions in absence and presence of Na-cyclamate.
2. Prevalence of interactions between polar groups of D(+) mannose and D(+) maltose monohydrate and ions of Na-cyclamate suggested by positive values of $\Delta_{trs}\ V_\phi^0$ and V_{AB}.
3. ASV values for (D(+) mannose and D(+) maltose monohydrate) in water and in (0.05, 0.15, 0.3) mol.kg^{-1} of Na-Cyclamate lies in range from (0.620-0.636) × 10^{-6} m^3.kg^{-1}. Hence studied combinations of aqueous solutions of (D(+) mannose and D(+) maltose monohydrate and Na-cyclamate under investigation show sweet taste.

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Conflict of interest

No conflict of interest

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