Studies in Densities & Apparent Molal Volumes of α & β Glucose at 25°c

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Abstract

This work was undertaken to study whether the density and apparent molal volume of α & β–Glucose are different or not as they have different positions of one of the hydroxyl group in α & β– Glucose, and if so, this difference may be related to the equatorial and axial position of the hydroxyl groups. α & β– Glucose were separated using acetic acid and pyridine respectively. Purity of α & β–Glucose was confirmed by measuring specific optical rotation as a function of time and also finding rate constant of mutarotation. From the demonstrative experiment it was proved that the density of α–Glucose during mutarotation decreased and apparent molal volume increased. From the density measurements of α and β–Glucose, we observed that the limiting apparent molal volume of α and β–Glucose are different. This leads to the conclusion that the solute solvent interactions are different for equatorial and axial positions of **OH^-** group of glucose.

Keywords: Densities, molal volume, α & β–Glucose, optical rotation, mutarotation

Introduction

Glucose, fructose, cane sugar, starch & cellulose were all considered to be hydrates of carbon and were therefore named as carbohydrates. e.g. glucose, fructose ($C_6H_{12}O_6$ or $C_6(H_2O)_6$), cane sugar ($C_{12}H_{22}O_{11}$ or $C_{12}(H_2O)_{11}$). But there are certain carbohydrates which cannot be represented as hydrates of carbon e.g. rhamnose $C_6H_{12}O_5$ etc. The term carbohydrate now includes all poly-hydroxy aldehydes and ketones along with substances which yield these on hydrolysis. Carbohydrates are further classified as sugars and non-sugars e.g. glucose, fructose and cane sugar are sugars and starch, cellulose etc. are non-sugars.

Carbohydrates play a very important role in influencing biological processes in animal and plant life. Normally 60-90 mg glucose is present in each 100 cc of blood. Muscles & other tissues absorb glucose from the blood to form glycogen, which by breaking down through many complex reactions provides energy to operate tissue mechanisms. Blood glucose serves as direct food for brain tissues.

Understanding the behavior of carbohydrates in dilute aqueous solutions is of utmost importance in biology and medicine. This behavior like other compounds can be understood by measuring thermodynamic properties in dilute solutions, like limiting apparent molal volumes, specific heats, temperature of maximum density, adiabatic compressibility etc. It has been pointed out earlier[1,2] that the hydration of carbohydrates depends upon the percentage of axial and equatorial hydroxyl groups and it is more favorable when the hydroxyl group is at equatorial position. Considerable work has been carried out on such properties of aqueous solutions of carbohydrates but at higher concentration range[3-7]. Such thermodynamic measurements at high concentration cannot be used to obtain reliable extrapolated limiting parameters[8], were the first to carry out thermodynamic measurements of some carbohydrates at 5°C and 25°C in low concentration region e.g. ribose, galactose, glucose, methyl pyranosides & cyclic

ethers. etc. From density and sound velocity measurements[9] of glucose, fructose, galactose, sucrose, lactose, α-methyl glucoside and β -methyl glucoside in dilute aqueous solutions limiting apparent molal volumes(ϕ_v^o) and limiting apparent molal compressibilities(ϕ_k^o) were evaluated.

The pyranose structure having 6 membered ring with oxygen as one of the atoms is applicable to nearly all sugars and is supported by X-ray analysis and accordingly two stereo-isomers of glucose are called as α & β–Glucose. One of the hydroxyl(OH) group in α–Glucose is at axial position and in β–Glucose it is at equatorial position, remaining structure is identical in both the cases. α–Glucose (38%) which has a specific optical rotation of +110.0°, when dissolved in water is converted gradually into a mixture which has a stable optical rotation of 52.56°. Similarly β–Glucose (62%) with the initial rotating power of +19.7° is converted into the same mixture. This change in specific rotation of an optically active solution without any change in other properties is known as mutarotation.

Due to difference of one of the hydroxyl group in α & β–Glucose, some changes might be expected in density & apparent molal volumes of their solutions. And if so, this difference could be related to the equatorial and axial position of the hydroxyl group. This work was undertaken to study whether the density & apparent molal volume of α & β–Glucose vary or not, if so up to what extent.

Materials and Methods

D-glucose, Acetic acid, Pyridine & ethyl alcohol used in the present work were of AR or GR grade. Acetic acid was first made moisture free by freezing it in ice bath and further it was purified by distillation. Ethanol was purified by dehydration with freshly ignited calcium oxide and then by reflux followed by distillation.

***Preparation of α–Glucose using acetic acid*:** Saturated aqueous solution of 100g D-glucose was prepared by heating. After filtering this hot solution, gradually 125ml acetic acid was added to the filtrate and about after 1 hour α–Glucose separates out. α–Glucose so obtained was then washed repeatedly using dried pure ethyl alcohol and dried in vacuum oven and then stored in vacuum desiccator.

***Preparation of β–Glucose using pyridine*:** 150g of D-glucose mixed with 150ml pure pyridine was refluxed for 3 hours. The hot reaction mixture was filtered quickly and to the filtrate during cooling when becomes viscous 100-120ml pure pyridine was added to get more yield of β–Glucose. The yield was filtered and washed repeatedly using dried pure ethyl alcohol for the complete removal of pyridine. β–Glucose so obtained was dried in vacuum oven and then stored in vacuum desiccator.

Apparent molal volume (ϕ_v) is given by, $$\phi_v = \frac{1000(d_0 - d)}{m \cdot d \cdot d_0} + \frac{M_2}{d} \quad \ldots (1)$$

Where, d – density of solution, d_o – density of solvent,
m – molality of solute M_2 – molecular weight of solute

Specific rotation, $(\alpha)_\lambda^t$ at t°C & at wavelength 'λ' by polarimeter is found out by

$$(\alpha)_\lambda^t = \frac{100 \times a}{l \times d} \quad \ldots (2)$$

Where, a – angle of rotation *l*– length of polarimeter tube in dm
d – solute per 100 g of solution

Mutarotation of α– & β–Glucose occurs by first order kinetics hence rate of disappearance of α– & β–Glucose is given by

$$-\frac{d_c}{d_t} = KC \qquad \ldots (3)$$

On integration we get $$Log\frac{C_0}{C} = \frac{kt}{2.303} \qquad \ldots (4)$$

Where, C_o and C are concentrations of reactants at time '0' and 't' respectively.

Using the values of rate constants[10] at 25°C, $k_\alpha = 0.5242 \times 10^{-4}$ sec^{-1} and $k_\beta = 0.9118 \times 10^{-1}$ sec^{-1} and equation (4) concentrations of α & β–Glucose was found separately at time 't' during mutarotation. The rate constant of mutarotation was found out by observing specific rotation as a function of time and using the following first order kinetics equation (5)

$$k_\alpha + k_\beta = \frac{2.303}{t} Log\frac{\alpha_\infty - \alpha_0}{\alpha_\infty - \alpha_t} \qquad \ldots (5)$$

Where, α_∞ - specific rotation at '∞' time, α_t – specific rotation at time 't'

α_o – specific rotation at time '0' which was obtained by extrapolating the graph to t = 0

Relative mole fraction of α– & β–Glucose at time 't' is given by equation (6)

$$x_1 = \frac{m_\alpha}{m_\alpha + m_\beta} \quad \text{and} \quad x_1 = \frac{m_\beta}{m_\alpha + m_\beta} \qquad \ldots(6)$$

Where, x_1 and x_2 are relative mole fractions of α– & β–Glucose respectively at time 't'.

m_α and m_β are relative mole fractions of α– & β–Glucose respectively at time 't'.

The limiting apparent molal volume of α– & β–Glucose individually was found out by extrapolation of apparent molal volume of α– & β–Glucose versus molality to zero concentration, the points at low concentration, which deviated considerably from linearity were not considered. The same procedure was followed[8] expecting the possibility of systematic error at low concentration due to dissolved air in the solution. For this, a required value of apparent molal volume ($\phi_{v.app}$) of α– & β–Glucose individually was found by solving following two sets of simultaneous equation (7).

$$\phi_{v.app} = x_1 . \phi_{v.\alpha g} + x_2 . \phi_{v.\beta g} \qquad \ldots(7)$$

Where, $\phi_{v.\alpha g}$ & $\phi_{v.\beta g}$ are apparent molal volume of α– & β–Glucose respectively.

Single pan float method[11] (using a Sartorious model-2474, Germany make) with semi-micro balance having facility to weigh below the pan was adopted, which can read to an accuracy up to 0.01 mg. A glass plunger was suspended by a thin nylon thread into double distilled water (about 1850g) kept in a stainless steel cylinder. The steel cylinder was kept in a well insulated and covered constant temperature bath (capacity 30L) whose temperature was maintained at 25°C by circulating water-methanol mixture from a MK-70 cryostat through large copper coils kept in the bath.

Experiment to see if densities of α & β–Glucose changes or not: Double distilled water (1854.577g) was taken in cylinder and the weight of plunger in water was noted. Then 12.6983g of α–Glucose was added to water in the cylinder and weight of plunger was noted for different time and observations were noted (Table.1). From this experiment it was proved that the density of α–Glucose during mutarotation decreased and apparent molal volume increased. Hence, there ought to be increase in density and decrease in apparent molal volume of β–Glucose during mutarotation.

Table 1: To see whether density of α– & β–Glucose changes during muta-rotation or not

Temperature of thermostat = 25°C
Weight of water taken in cylinder = 1854.5770 g
Weight of plunger in air = 193.65748 g
Weight of plunger in water = 27.80435 g
Therefore, Volume of plunger = 166.35685 cc
Weight of glucose taken = 12.6983 g
Molality of solution = 0.0380051

Sr. no.	Time when weight of plunger was noted (s)	Weight of plunger in solution (g)	Density (g/cc)	ϕ_v (cc/mole)
1	305	27.36350	0.9996220	110.2624
2	580	27.36536	0.9996108	110.5594
3	825	27.36668	0.9996029	110.7688
4	1320	27.36803	0.9995948	110.9853
5	1805	27.36860	0.9995914	111.0737
6	2435	27.36910	0.9995884	111.1533

***Purity and rate constant of Mutarotation of α -Glucose*:** Purity of α–Glucose was confirmed by measuring optical rotation and also finding rate constant of mutarotation by Polarimeter (England made, Least count = 0.01°, tube length = 2 dm). This was done in two runs and specific rotation was plotted against time with neglecting little error. For this run, 0.6634g of α–Glucose was dissolved in distilled water (1.3268% solution). Then the angle of rotation for different time intervals was measured. Specific rotation and rate of mutarotation were calculated using eq. (2) and eqn. (5) respectively (Table 2).

Table 2: α - Glucose - Purity and Rate constant of Mutarotation (2 Runs)

Run	Sr. no.	Time in Sec	Angle of rotation	Specific rotation	$\frac{\alpha_\infty - \alpha_0}{\alpha_\infty - \alpha_t}$	$k_\alpha + k_\beta$ (10000/Sec)	Mean $k_\alpha + k_\beta$ per sec
I	1	255	2.86	107.8	1.042	1.604	2.8218×10^{-4}
	2	605	2.68	100.81	1.199	2.972	
	3	860	2.61	98.17	1.268	2.764	
	4	1140	2.50	94.21	1.393	2.907	
	5	1420	2.44	91.95	1.476	2.740	
	6	1725	2.40	90.26	1.544	2.519	
	7	2525	2.01	75.75	2.569	3.722	
	8	3090	1.96	73.86	2.812	3.347	
	9	∞	1.43	53.89			
II	1	90	7.97	108.47	1.019	2.072	2.1789×10^{-4}
	2	705	7.45	101.39	1.168	2.201	
	3	1095	7.25	98.60	1.240	1.964	
	4	1790	6.73	91.52	1.469	2.148	
	5	2445	6.27	85.33	1.753	2.296	
	6	3120	5.96	81.04	2.023	2.258	
	7	3685	5.65	76.89	2.377	2.349	
	8	5105	5.30	72.06	2.986	2.143	
	9	∞	3.91	53.21			

***Purity and rate constant of Mutarotation of β-Glucose*:** Purity of β–Glucose was confirmed by measuring optical rotation & also by finding rate constant of mutarotation This was also done in 2 runs and specific rotation was plotted against time. For this run, 0.8309g of β–Glucose was dissolved in distilled water (3.3236% solution). Then the angle of rotation for different time intervals was measured. Specific rotation and rate of mutarotation were calculated using eqns. (2) & (5) respectively (Table 3).

Table 3: β - Glucose - Purity and Rate constant of Mutarotation (2 Runs)

Run	Sr. no.	Time in Sec	Angle of rotation	Specific rotation	$\frac{\alpha_\infty - \alpha_0}{\alpha_\infty - \alpha_t}$	$k_\alpha + k_\beta$ (10000/Sec)	Mean $k_\alpha + k_\beta$ per sec
I	1	95	1.35	20.31	1.025	2.644	3.5669×10^{-4}
	2	500	1.55	23.32	1.133	2.489	
	3	790	1.76	26.45	1.270	3.029	
	4	1080	2.09	31.44	1.576	4.214	
	5	1500	2.16	32.49	1.660	3.381	
	6	1840	2.48	37.23	2.188	4.255	
	7	2385	2.73	40.99	2.924	4.499	
	8	3360	2.81	42.27	3.302	3.556	
	9	∞	3.47	52.16			
II	1	90	0.92	20.99	1.024	2.635	2.1789×10^{-4}
	2	380	1.09	24.75	1.164	3.999	
	3	810	1.31	29.88	1.431	4.424	
	4	1100	1.35	30.80	1.492	3.605	
	5	1515	1.55	35.36	1.895	4.219	
	6	2390	1.65	37.64	2.191	3.282	
	7	3050	1.78	40.61	2.751	3.318	
	8	4130	1.87	42.66	3.339	2.919	
	9	∞	2.29	52.24			

***Apparent molal volume of α & β - Glucose at 25°C*:**

For the measurement of density of α– & β–Glucose, double distilled water (about 1850g) was taken in cylinder and the weight of plunger in water was noted. α–Glucose (about 9-10g) was added to water in the cylinder and after proper mixing weight of plunger was noted. Then consecutively exactly known quantity of α–Glucose (about 2g) was mixed in situ and every time weight of plunger was noted. This was carried out in two runs (Table.4). Similar process was repeated for β–Glucose in two runs (Table.4).

Pairs of simultaneous equations using eqn.(7) for columns 6-8 and 14-16 of Table:4, each obtained by mutarotation of α & β–Glucose were solved to get apparent molal volume of α & β-Glucose $\phi_{v.\alpha g}$ and $\phi_{v.\beta g}$ respectively (column 17 & 18 of Table:4). Graph of apparent molal volume of α–Glucose for both the runs together against molality of α–Glucose when extrapolated to zero concentration, gave the limiting apparent molal volume of α– Glucose $\phi^o_{v.\alpha g}$. Similar graph was extrapolated for β–Glucose to zero concentration to get the limiting apparent molal volume of β- Glucose $\phi^o_{v.\beta g}$.

Table 4a: Limiting apparent molal volume of α– & during Mutarotation of α-Glucose.

Time in Sec	wt of Glucose in g	wt of plunger in solution	molality m	density in g/cc	ϕ_v cc/ mole	Relative molefraction of	
RUN I: Weight of water taken in the cylinder =1845.0156 g						α-Glucose	β-Glucose
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
255	8.9898	27.48044	0.02704	0.9990089	107.44	0.9867250	0.0132746
675	10.9669	27.41994	0.03299	0.9993726	109.56	0.9684165	0.0315834
985	13.0650	27.35204	0.03930	0.9997808	110.44	0.9582994	0.0417005
1265	15.0616	27.28482	0.04531	1.0001849	110.70	0.9488976	0.0511023
1600	17.0467	27.21678	0.05128	1.0005939	110.74	0.9395881	0.0604118
RUN II: Weight of water taken in the cylinder =1851.0427 g							
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
315	9.9982	27.45628	0.02998	0.9991541	109.79	0.9836224	0.0163775
590	12.0099	27.39015	0.03601	0.9995517	110.47	0.9725980	0.0274019
885	14.0439	27.32096	0.04211	0.9999676	110.62	0.9618446	0.0381553
1155	16.0883	27.25318	0.04824	1.0003751	110.94	0.9533414	0.0466605
1385	18.0554	27.18562	0.05414	1.0007810	110.91	0.9471407	0.0528592
1700	19.8758	27.12810	0.05960	1.0011270	111.39	0.9366214	0.0633785

Table 4b: Limiting apparent molal volume of β–Glucose during Mutarotation of β-Glucose

Time in Sec	wt of Glucose in g	wt of plunger in solution	molality m	density in g/cc	ϕ_v cc/ mole	Relative molefraction of		Solving eqn.(7) for colms 6-8 & 14-16	
RUN I: Weight of water taken in the cylinder =1853.6459 g						α-Glucose	β-Glucose	$\phi_{v\alpha g}$	$\phi_{v\beta g}$
9	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**
305	8.9897	27.49500	0.026919	0.9989213	110.47	0.027423	0.972577	107.40	110.56
565	10.9492	27.43049	0.032786	0.9993091	111.07	0.0448545	0.955145	109.51	111.14
820	12.9979	27.36226	0.038921	0.9997193	111.35	0.059261	0.940739	111.40	111.41
1085	14.9951	27.29489	0.044900	1.0001243	111.42	0.073608	0.926392	110.66	111.49
1345	16.9984	27.22696	0.050900	1.0005327	111.43	0.0864066	0.913594	110.69	111.50
RUN II: Weight of water taken in the cylinder =1857.7667 g									
9	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**
230	9.9379	27.45959	0.029787	0.9991342	110.0	0.0207506	0.979249	109.79	110.02
465	11.8332	27.39873	0.035468	0.9995001	110.87	0.0378256	0.962174	110.46	110.89
745	13.8846	27.32969	0.041617	0.9999151	111.07	0.0560347	0.943966	110.60	111.10
1030	15.8807	27.26157	0.047600	1.0003246	111.08	0.072989	0.92701	110.93	111.10
1360	17.8998	27.19270	0.053652	1.0007387	111.34	0.087926	0.912075	110.88	111.38
1635	19.2958	27.14737	0.057837	1.0010112	111.32	0.108128	0.891872	111.40	111.31

Results and Discussion:

Optically transparent α– & β–Glucose were separated by acetic acid and pyridine respectively. However, α–Glucose separated by ethyl alcohol cannot be used because its solution (even 0.5%) was opaque to sodium light used in Polarimeter.

Plot of specific rotation of α– & β–Glucose separately against time in second on extrapolation to zero time gave the values of optical rotation (at time t = 0 sec) which are in good agreement with the literature. Also the rate constant of mutarotation are in good agreement with the literature[12]. It indicates very good purity of α– & β–Glucose which were separated by acetic acid and pyridine respectively.

Demonstrative experiment proved that the density of α–Glucose during mutarotation decreased and apparent molal volume increased. Hence, we conclude that density and apparent molal volume of α and β–Glucose individually ought to be different. Thus by performing 2 runs for density measurement of α –Glucose (Table 4, column 1-8) and two runs for β–Glucose (Table 4, columns 9-16). We observed that the limiting apparent molal volume of α and β–Glucose are different. The values of $\phi^{o}_{v.\alpha g}$ & $\phi^{o}_{v.\beta g}$ are shown in Table: 5. This leads to the conclusion that the solute solvent interactions are different for equatorial and axial positions of **OH^-** group of glucose. In case of β–Glucose having **OH^-** group on equatorial position have higher limiting apparent molal volume than α–Glucose having **OH^-** group on axial position. Hence, from this work it is concluded that such type of difference in density & limiting apparent molal volume may be observed for various carbohydrates which have α & β–forms.

Table 5: Limiting apparent molal volume of α & β - Glucose.

Limiting apparent molal volume of α – Glucose. $\phi^{o}_{v.\alpha g}$	Limiting apparent molal volume of β - Glucose. $\phi^{o}_{v.\beta g}$
110.00 cc/mole	111.25 cc/mole

Measurements[13] on (a) the vapour pressures of aqueous solutions of glucose from 25-65 ^{o}C and up to a mole fraction of glucose of 0.195. (b) the heat of dilution at 25 ^{o}C up to a mole fraction of 0.245 (c) the heat capacity of glucose solution at 25 ^{o}C (d) heats of solutions at 25 ^{o}C of α–glucose, β–Glucose and α–glucose monohydrate and (e) densities of glucose from 25-65 ^{o}C up to a mole fraction of 0.270. All the solutions studied here were equilibrium mixtures of optical isomers, they had not tried for study of separate isomers.

From optical rotation (OR) measurements[14] of different optical isomers of glucose in aqueous solutions, α structures showed large positive contribution to OR, while the β structures gave both positive and negative contributions.

Densities and viscosities measurements of D-glucose, D-fructose, sucrose and maltose were used[15] to evaluate limiting apparent molar volume. The results showed strong solute -solvent interaction indicating their water structure making propensity in aqueous solution due to hydrophobic hydration and hydrogen bonding between solute and water molecules. They also found linear behavior of ϕ_v as a function of concentration. Different thermodynamic and spectroscopic study[16-18] showed that the hydration of carbohydrate did not depend only on hydroxyl group & potential site of hydrogen bonding, but also depend on their relative orientation (axial or equatorial). Further investigations on velocity and sound in the solutions of α and β–glucose are expected from which hydration characteristics and limiting apparent molal compressibilities can be studied.

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