

Chapter VI

Study to Explore Diverse Interactions By Physicochemical Contrivance Of An Ionic Liquid In Aqueous Oligosaccharides

ABSTRACT

In this work, the interaction phenomena of an ionic liquid 1-butyl-1-methylpyrrolidinium chloride [bmp]Cl has been studied in different concentrations of aqueous D(-)fructose and D(+)galactose solutions at three different temperatures. The limiting molal conductivities, association constants of the ion have been evaluated. The limiting apparent molal volumes, experimental slopes and the limiting partial molal transfer volumes has been derived from density calculation. The association constant has also been determined from conductivity study and other parameters like Gibbs free energy (ΔG_A^0), enthalpy (ΔH_A^0) and entropy (ΔS_A^0) of ion-pair formation have been calculated. $^1\text{H NMR}$ spectroscopic study does not show any kind of strong interactions between IL and carbohydrates but, their changes in terms of size and structure of carbohydrates and IL have been discussed here. By means of the interaction between IL and biomolecules, the potential toxicity of ILs may arise.

Keywords: Green solvent; Limiting molal conductivities; ion–solvent and ion–ion interaction; Thermodynamic functions, NMR study, Potential toxicity

1. INTRODUCTION

In the era of globalisation, Ionic liquids (IL) have been emerged as “green” and environment friendly solvents [203, 204] for their use in the industrial manufacture of chemicals. Ionic liquids are also being used for organic synthesis, catalysis, electrochemical devices and solvent extraction of a variety of compounds. The interest in ionic liquids was initiated because of their advantageous physicochemical properties such as negligible vapour pressure, high thermal and electrochemical stability, high solvating power etc. [97, 205, 206]. [bmp]Cl are widely used in catalysts, battery electrolytes, and electrochemical relevances other than batteries.

Carbohydrates (such as glucose, fructose, galactose etc.) are most important substances to all living organisms. They act as a ubiquitous fuel for biological processes to supply necessary energy. D(+)galactose and D(-)fructose are very significant variety of saccharide. In spite of the “green” aspects of ILs, the potential toxicity of the ILs released into the environment cannot be overlooked [207]. Since ILs are highly stable. in water, these can cause health hazards by gathering in the ecological atmosphere and organisms. So, it is very important to determine the potential toxicity of IL originate from the interface between ILs and biomolecules.

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In this present case, an attempt has been made to reveal the nature of interactions prevailing an ionic liquid in aqueous carbohydrates [D(-)fructose and D(+)-galactose] solutions from conductometric, volumetric, viscometric and NMR spectroscopic approaches. Aim of the present work is to study the molecular interactions of IL in aqueous solutions of carbohydrates by physicochemical and thermodynamical studies. Such study helps in better understanding of the interactions occurring between carbohydrate molecules and entities present in mixed aqueous medium in the living cells through thermodynamics and transport properties.

2. Experimental

2.1 Source and purity of samples

1-butyl-1-methylpyrrolidinium chloride (ionic liquid) was purchased from Sigma-Aldrich, Germany and was used without further purification. The mass fraction purity of the IL, 1-butyl-1-methylpyrrolidinium chloride [bmp]Cl was $\geq 99\%$.

D(-)fructose and D(+)-galactose were procured from Thomas Baker, Mumbai. The mass fraction purity of D(-)fructose and D(+)-galactose was $\geq 99.4\%$ and 99.9% respectively. IL, D(-)fructose and D(+)-galactose were dried in vacuum desiccator over P_2O_5 at room temperature for at least 72 hours.

3. Results and Discussion

Density (ρ), viscosity (η) and relative permittivity (ϵ) values are given in **Table.1**.

Conductivity measurements have been carried out to determine the association behaviour and ion-solvent interactions [208, 209] of the ionic liquid, [bmp]Cl, in (0.2, 0.4 and 0.6) mol kg⁻¹ aqueous D(-)fructose and D(+)-galactose solutions at temperatures ranging from (298.15–308.15)K. The concentrations and molar conductances (Λ) of IL in aqueous solution of D(-)fructose and D(+)-galactose at different temperatures are given in Table. 2. The molar conductance (Λ) has been obtained from the specific conductance (κ) value using the following equation.

$$\Lambda = (1000 \kappa) / m \quad (1)$$

Linear conductance curves (Λ versus \sqrt{m}) were obtained for the electrolyte in aq. solution of D(-)fructose. D(+)-Galactose, extrapolation of $\sqrt{m} = 0$ evaluated the starting limiting molar conductance for the electrolyte. The values of K_A , Λ_0 and R obtained by this procedure are given in **Table.3**.

Table.1. Density (ρ), viscosity (η) and relative permittivity (ϵ) of the different concentration (m) of aqueous D(-)fructose and D(+)galactose at 298.15, 303.15 and 308.15 K^a respectively.

T (K)	$\rho \cdot 10^{-3}/\text{kg m}^{-3}$	$\eta/\text{mPa s}$	E
$m_{\text{D(-)fructose}}=0.2 \text{ mol kg}^{-1}$			
298.15	1.0039	0.93	78.1
303.15	1.0025	0.91	76.3
308.15	1.0018	0.89	74.5
$m_{\text{D(-)fructose}}=0.4 \text{ mol kg}^{-1}$			
298.15	1.0051	0.93	77.4
303.15	1.0028	0.91	75.5
308.15	1.0021	0.90	73.8
$m_{\text{D(-)fructose}}=0.6 \text{ mol kg}^{-1}$			
298.15	1.0062	0.93	76.8
303.15	1.0049	0.92	74.9
308.15	1.0027	0.90	73.1
$m_{\text{D(+)galactose}}=0.2 \text{ mol kg}^{-1}$			
298.15	1.0037	0.93	78.1
303.15	1.0023	0.91	76.3
308.15	1.0015	0.90	74.5
$m_{\text{D(+)galactose}}=0.4 \text{ mol kg}^{-1}$			
298.15	1.0045	0.93	77.4
303.15	1.0025	0.92	75.5
308.15	1.0020	0.90	73.8
$m_{\text{D(+)galactose}}=0.6 \text{ mol kg}^{-1}$			
298.15	1.0059	0.93	76.8
303.15	1.0047	0.92	74.9
308.15	1.0025	0.90	73.1

^a Standard uncertainties u are: $u(\rho) = \pm 5 \times 10^{-5} \text{ g} \cdot \text{cm}^{-3}$, $u(\eta) = \pm 1 \%$ and $u(T) = \pm 0.01 \text{ K}$

3.1. Ion-pair Formation

The conductivity data of taken IL in aqueous solution of D(-)fructose and D(+)galactose at different temperatures were analyzed using the Fuoss conductance equation [210]. With a given set of conductivity values (m_j , A_j ; $j = 1, \dots, n$), three adjustable parameters, i.e., A_0 , K_A and R have been derived from the Fuoss equation. Here, A_0 is the limiting molar conductance, K_A is the association constant and R is the association distance, i.e., the maximum centre to centre distance between the ions in the solvent separated ion-pairs. There is no precise method [211] for determining the R value but in order to treat the data in our system, R value is assumed to be, $R = a + d$, where a is the sum of the crystallographic radii of the ions and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance, d is given by [212].

$$d = 1.183 (M / \rho)^{1/3} \quad (2)$$

where, M is the molecular mass and ρ is the density of the solvent.

Thus, the Fuoss conductance equation may be represented as follows:

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$$A = P\Lambda_o[(1 + R_X) + E_L] \quad (3)$$

$$P = 1 - \alpha(1 - \gamma) \quad (4)$$

$$\gamma = 1 - K_A m \gamma^2 f^2 \quad (5)$$

$$-\ln f = \beta \kappa / 2(1 + \kappa R) \quad (6)$$

$$\beta = e^2 / (\epsilon_r k_B T) \quad (7)$$

$$K_A = K_R / (1 - \alpha) = K_R / (1 + K_S) \quad (8)$$

where, R_X is the relaxation field effect, E_L is the electrophoretic counter current, k is the radius of the ion atmosphere, ϵ is the relative permittivity of the solvent mixture, e is the electron charge, c is the molarity of the solution, k_B is the Boltzmann constant, K_S is the association constant of the contact-pairs, K_R is the association constant of the solvent-separated pairs, γ is the fraction of solute present as unpaired ion, α is the fraction of contact pairs, f is the activity coefficient, T is the absolute temperature and β is twice the Bjerrum distance.

The initial Λ_0 values for the iteration procedure are obtained from Shedlovsky extrapolation of the data [213]. Input for the program is the no. of data, n , followed by ϵ , η (viscosity of the solvent mixture), initial Λ_0 value, T , ρ (density of the solvent mixture), mole fraction of the first component, molar masses, M_1 and M_2 along with m_j , A_j values where $j = 1, 2, \dots, n$ and an instruction to cover preselected range of R values.

In practice, calculations are performed by finding the values of Λ_0 and α which minimize the standard deviation, δ , whereby

$$\delta^2 = \sum [A_j(cal) - A_j(obs)]^2 / (n - m) \quad (9)$$

for a sequence of R values and then plotting δ against R , the best-fit R corresponds to the minimum of the δ - R versus R curve. So, an approximate sum is made over a fairly wide range of R values using 0.1 increment to locate the minimum but no significant minima is found in the δ - R curves. Finally, the corresponding limiting molal conductance (Λ_o), association constant (K_A), co-sphere diameter (R) and standard deviations of experimental Λ (δ) obtained from Fuoss conductance equation for [bmp]Cl in aqueous solution of D(-)fructose and D(+)galactose at 298.15 K, 303.15 K and 308.15 K respectively are given in **Table.3**.

3.2. Limiting molal conductivities

Assessment of **Table.2.** and **Table.3.** allocate that the Λ_o values of the ionic liquid decrease with increasing the concentration of D(-)fructose and D(+)galactose. This can be ascribed to the facts that with increase in D(-)fructose and D(+)galactose concentration (i) the microscopic viscosity of the mixtures increases thereby the mobility of ions decreases, and (ii) the solvated radii of ions become larger through an enhancement in the interactions between ionic liquid and D(-

)fructose and D(+)-galactose solution therefore, the mobility of ions decreases [214]. On the other hand, the Λ_0 values increase from D(-)-fructose to D(+)-galactose. Due to higher viscosity value of D(-)-fructose than D(+)-galactose Λ_0 values increase in D(+)-galactose than in D(-)-fructose. Λ_0 values increase in every solution with increase of temperature. With increasing temperature mobility of the concerned ions in solution increases, so Λ_0 values increase.

Table. 2. Molar conductivities (Λ) of [bmp]Cl in aqueous D(-)-fructose solutions as a function of ionic liquid molality (m) at different temperatures.

$c \cdot 10^4 /$ $\text{mol} \cdot \text{dm}^{-3}$	$\Lambda \cdot 10^4 /$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$c \cdot 10^4 /$ $\text{mol} \cdot \text{dm}^{-3}$	$\Lambda \cdot 10^4 /$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$c \cdot 10^4 /$ $\text{mol} \cdot \text{dm}^{-3}$	$\Lambda \cdot 10^4 /$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$
		T=303.15		T=308.15K	
T=298.15K					
m _{D(-)fructose} =0.2 mol kg ⁻¹					
0.0114	101.10	0.0122	104.58	0.0132	107.60
0.0173	99.13	0.0223	101.91	0.0251	104.57
0.0239	96.45	0.0309	99.93	0.0320	103.13
0.0296	94.32	0.0383	98.20	0.0398	101.50
0.0345	92.40	0.0447	96.79	0.0469	99.90
0.0389	91.01	0.0503	95.34	0.0523	97.40
0.0427	89.91	0.0552	94.33	0.0579	96.80
0.0464	88.51	0.0596	93.18	0.0613	95.00
0.0512	87.91	0.0635	92.21	0.0647	94.26
0.0551	86.94	0.0670	91.44	0.0684	93.89
0.0593	85.50	0.0702	90.53	0.0715	92.03
0.0672	84.29	0.0731	89.91	0.0750	91.59
0.0715	83.11	0.0757	89.12	0.0765	90.53
0.0763	81.82	0.0782	88.09	0.0792	89.05
0.0841	80.20	0.0804	87.58	0.0815	89.78
m _{D(-)fructose} =0.4 mol kg ⁻¹					
0.0121	99.43	0.0138	102.37	0.0142	105.85
0.0187	97.40	0.0235	100.75	0.0216	104.70
0.0241	95.04	0.0313	99.55	0.0285	103.58
0.0310	93.62	0.0385	97.16	0.0346	102.62
0.0353	92.56	0.0465	95.91	0.0388	101.66
0.0395	90.90	0.0513	94.12	0.0438	100.70
0.0443	90.42	0.0544	93.40	0.0491	99.67
0.0475	88.35	0.0596	93.95	0.0551	97.57
0.0496	87.45	0.0635	92.88	0.0617	95.46
0.0542	85.76	0.0674	90.18	0.0675	93.24
0.0595	84.67	0.0715	89.52	0.0707	91.72
0.0657	83.63	0.0742	88.87	0.0731	89.29
0.0713	82.73	0.0774	88.09	0.0779	89.84
0.0765	81.62	0.0812	87.48	0.0821	88.79
0.0846	79.38	0.0851	86.83	0.0852	88.30
m _{D(-)fructose} =0.6 mol kg ⁻¹					
0.0128	95.51	0.0143	98.99	0.0152	102.57
0.0185	94.48	0.0242	97.04	0.0271	100.17
0.0229	93.20	0.0316	95.70	0.0331	99.03
0.0282	91.54	0.0386	94.52	0.0423	97.20
0.0313	90.40	0.0451	93.13	0.0481	96.00

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0.0351	89.27	0.0503	92.03	0.0542	94.75
0.0420	87.31	0.0557	91.06	0.0598	93.33
0.0456	86.00	0.0596	90.21	0.0631	92.92
0.0494	85.65	0.0635	89.45	0.0656	92.24
0.0499	84.91	0.0674	88.51	0.0699	90.17
0.0540	83.18	0.0730	87.35	0.0731	89.54
0.0591	82.23	0.0756	86.55	0.0763	88.91
0.0664	81.26	0.0785	86.05	0.0782	88.15
0.0719	80.09	0.0820	85.17	0.0819	87.99
0.0786	78.08	0.0841	84.73	0.0860	87.57

Table 3. Molar conductivities (Λ) of [bmp]Cl in aqueous D(+)-galactose solutions as a function of ionic liquid molality (m) at different temperatures.

$c \cdot 10^4 /$ $\text{mol} \cdot \text{dm}^{-3}$	$\Lambda \cdot 10^4 /$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$c \cdot 10^4 /$ $\text{mol} \cdot \text{dm}^{-3}$	$\Lambda \cdot 10^4 /$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$	$c \cdot 10^4 /$ $\text{mol} \cdot \text{dm}^{-3}$	$\Lambda \cdot 10^4 /$ $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$
T=298.15K		T=303.15		T=308.15K	
$m_{\text{D}(+)\text{galactose}} = 0.2 \text{ mol kg}^{-1}$					
0.0118	102.50	0.0142	105.13	0.0129	108.95
0.0233	99.52	0.0254	102.86	0.0241	106.07
0.0311	97.58	0.0330	100.97	0.0303	105.43
0.0381	96.24	0.0396	99.54	0.0380	104.35
0.0445	94.71	0.0482	98.65	0.0449	102.63
0.0525	93.12	0.0521	97.54	0.0515	101.80
0.0558	92.12	0.0582	96.40	0.0560	100.96
0.0594	91.65	0.0616	95.20	0.0602	99.94
0.0638	90.48	0.0650	94.48	0.0629	99.06
0.0674	89.24	0.0687	93.74	0.0662	98.99
0.0715	88.10	0.0726	92.03	0.0707	98.76
0.0740	87.19	0.0752	91.84	0.0732	97.09
0.0774	85.91	0.0765	91.23	0.0749	96.82
0.0787	85.22	0.0792	91.95	0.0782	95.50
0.0815	84.76	0.0815	90.40	0.0821	94.60
$m_{\text{D}(+)\text{galactose}} = 0.4 \text{ mol kg}^{-1}$					
0.0124	100.33	0.0129	103.49	0.0142	107.87
0.0173	98.93	0.0196	102.40	0.0265	105.27
0.0249	97.37	0.0279	101.12	0.0325	104.03
0.0311	95.32	0.0352	99.76	0.0409	102.22
0.0355	94.46	0.0418	98.68	0.0464	101.11
0.0395	92.60	0.0472	97.80	0.0531	99.60
0.0443	91.50	0.0518	96.92	0.0567	98.89
0.0475	90.50	0.0562	95.40	0.0604	98.06
0.0496	90.06	0.0609	94.53	0.0654	96.85
0.0542	89.86	0.0670	93.51	0.0698	95.93
0.0599	88.77	0.0705	92.92	0.0727	95.20
0.0657	86.43	0.0736	91.25	0.0758	94.63
0.0721	85.63	0.0770	90.55	0.0784	94.24
0.0765	85.04	0.0807	89.01	0.0821	93.60
0.0844	83.30	0.0845	89.33	0.0880	92.13
$m_{\text{D}(+)\text{galactose}} = 0.6 \text{ mol kg}^{-1}$					
0.0153	97.11	0.0140	101.41	0.0150	105.25
0.0253	94.91	0.0215	99.83	0.0259	102.97
0.0331	92.80	0.0316	97.63	0.0329	101.53
0.0423	91.75	0.0371	96.60	0.0384	100.41

0.0481	90.28	0.0429	95.64	0.0430	99.19
0.0542	89.07	0.0494	94.32	0.0487	97.94
0.0598	88.11	0.0530	93.37	0.0527	97.11
0.0631	87.23	0.0583	92.44	0.0581	96.00
0.0656	86.21	0.0629	91.49	0.0624	95.17
0.0699	85.23	0.0652	91.03	0.0667	94.22
0.0731	84.16	0.0714	89.65	0.0715	92.95
0.0763	83.03	0.0744	88.93	0.0758	92.11
0.0782	81.93	0.0775	88.15	0.0785	91.67
0.0819	80.99	0.0812	87.71	0.0823	90.72
0.0862	80.33	0.0854	86.82	0.0859	90.08

3.3. Thermodynamic of the ion-association process

Values of the association constant (K_A) for the ionic liquids in aqueous D(-)fructose and D(+)galactose solutions are shown in **Table.4**. It is obvious that at a fixed concentration of D(-)fructose and D(+)galactose, the K_A values decrease from D(-)fructose to D(+)galactose and also decrease with increasing temperature in each solution. The association constant (K_A) for the ionic association reaction can serve to study the thermodynamic of this process. Consequently, the standard Gibbs energy (G_A^0) for the ion-association process were calculated according to the following equation [215]

$$\Delta G_A^o = -RT \ln K_A \quad (10)$$

The obtained values of the standard Gibbs energy are collected in Table. 6. Table. 6 indicates that the ion-association process exhibits a negative value of (G_A^0) and becomes more negative in D(+)galactose than in D(-)fructose. This indicates that ion-association process is more feasible in D(+)galactose solution. Walden product value (**Table.6.**) shows that ionic mobility is higher in case of D(+)galactose solution than in D(-)fructose solution and ionic mobility increases with increasing temperature.

Temperature-dependent of G_A^0 was expressed with the help of a polynomial[216]

$$\Delta G_A^o(T) = A_0 + A_1(298.15 - T) + A_2(298.15 - T)^2 \quad (11)$$

Entropy and enthalpy of ion association have been obtained as follows

$$\Delta S_A^0(T) = - \left(\frac{\partial \Delta G_A^0(T)}{\partial T} \right)_P = A_1 + 2A_2(298.15 - T) \quad (12)$$

$$\Delta H_A^0(T) = \Delta G_A^0(T) + T \Delta S_A^0(T) = A_0 + 298.15A_1 + (298.15^2 - T^2)A_2 \quad (13)$$

The values of the coefficients A_0 , A_1 and A_2 at different solvent compositions are given in **Table.5**. The calculated thermodynamic functions of IL in D(-)fructose and D(+)galactose solutions are listed in **Table.6.** and are represented graphically by **Fig.1.**, **Fig.2.** and **Fig.3.**

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respectively. **Table.6.** indicates that the ion-association process exhibits a negative value of ΔG_A^0 and becomes more negative with increasing temperature proposing the spontaneity and feasibility of the association process at high temperatures. In all cases, the ΔS_A^0 values are positive over the whole temperature range. The positive ΔS_A^0 values may be attributed to the increasing number of degrees of freedom due to the release of solvent molecules from hydration shells as the association takes place. In other words, the solvation of the individual ions is weakened as soon as these ion-pairs are formed. The positive contribution of entropy resulting from the dehydration of ions during the association process dominates over the negative contribution from the formation ion-pairs. It should be noted that the entropy term ($T\Delta S_A^0$) is sufficiently positive to exceed the positive contribution of the enthalpy (ΔH_A^0). Consequently, the ion-association process exhibits negative values of ΔG_A^0 and the process is driven by the change in entropy. Assessment of **Table.6.** also indicates that in case of [bmp]Cl in both aqueous solution of D(-)fructose than in D(+)galactose enthalpy decreases with increasing temperature and changes its sign from positive to negative at 308.15 K. This means that the association process is endothermic at lower temperature and exothermic at higher temperature. Furthermore, it means that ion-pair formation is entropy-driven at low temperatures, while it changes to enthalpy-driven process with increasing temperature. Enthalpy value of the IL is higher in case of D(-)fructose than in D(+)galactose. This means that the association process is more feasible in D(+)galactose than in D(-)fructose. It was observed that the ion-association process exhibits a negative value of ΔG_A^0 and becomes more negative with increasing temperature proposing the spontaneity and feasibility of the association at high temperatures.

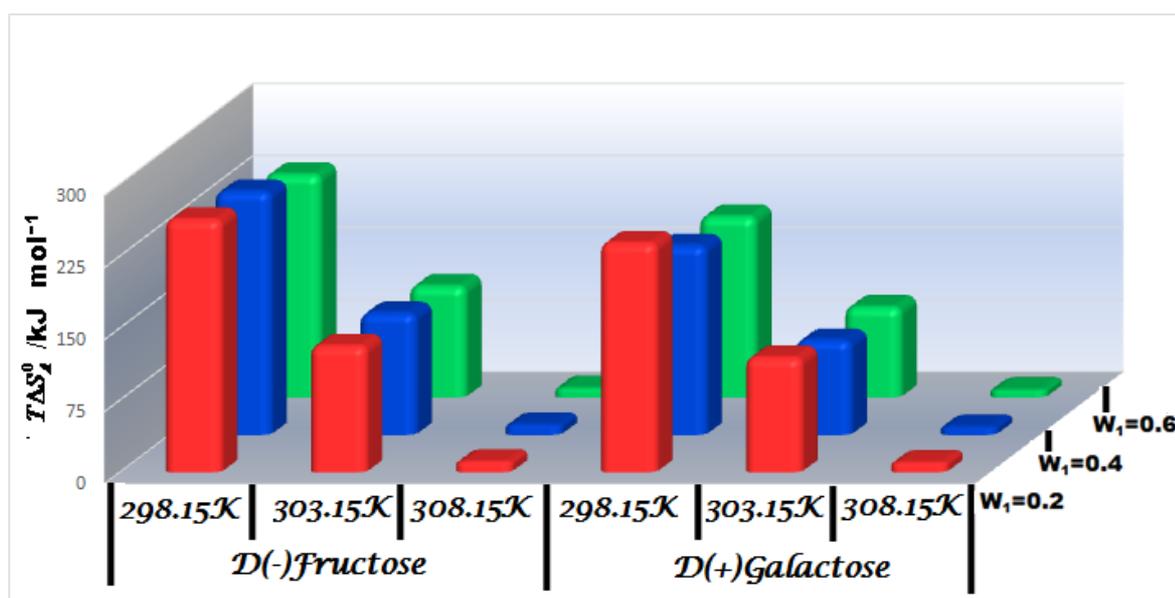


Fig.1. Plot of $T\Delta S_A^0$ of IL in different mass fractions of aqueous D(-)fructose and D(+)galactose solution respectively at different temperatures.

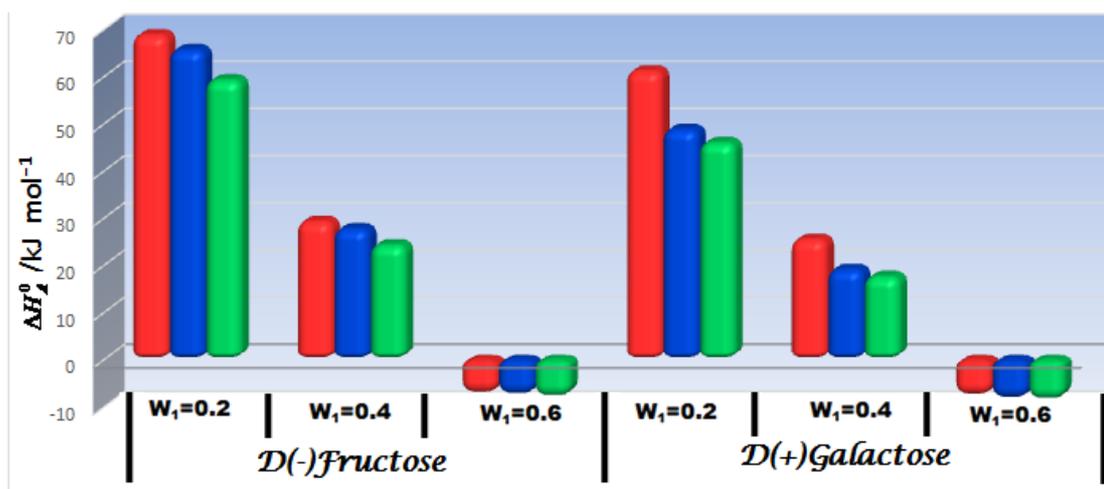


Fig.2. Plot of ΔH_A^0 of IL in different mass fractions of aqueous D(-)fructose and D(+)galactose solution respectively at 298.15 K (red), 303.15 K (blue) and 308.15 K (green) respectively.

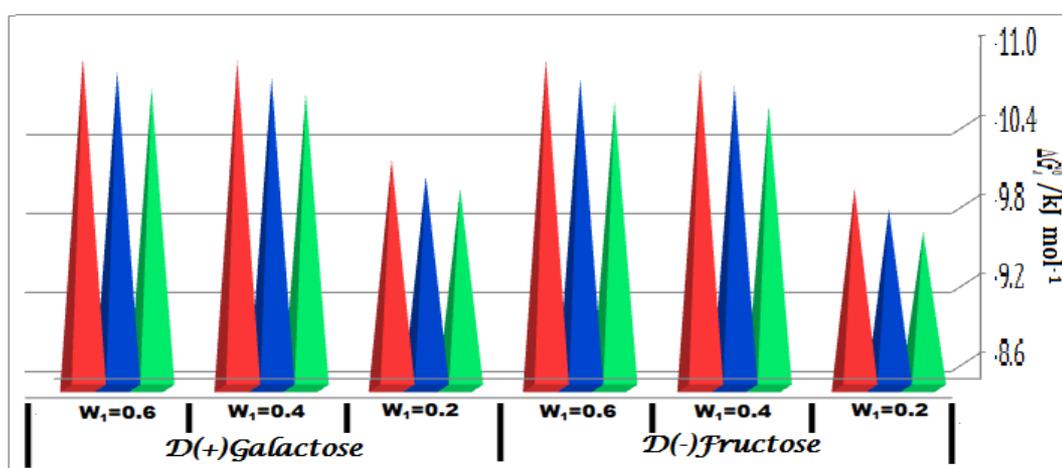


Fig. 3. Plot of ΔG_A^0 of IL in different mass fraction of aqueous D(-)fructose and D(+)galactose solution respectively at 298.15 K (red), 303.15 K (blue) and 308.15 K (green) respectively.

Table.4. Ion association constants (K_A), limiting molar conductivities(Λ_0), distance parameters (R),Walden product ($\Lambda_0 \cdot \eta$) and standard deviations (δ) obtained from Fuoss conductance equation of IL in aqueous D(-)fructose and D(+)galactose solutions as a function of ionic liquid molality (m) at different temperatures.

T (K)	$K_A(\text{dm}^3 \text{mol}^{-1})$	$\Lambda_0(\text{S cm}^2 \text{mol}^{-1})$	$10^{10}R(\text{m})$	$\Lambda_0 \cdot \eta(\text{S cm}^2 \text{mPa s mol}^{-1})$	δ
$m_{\text{D(-)fructose}} = 0.2 \text{ mol kg}^{-1}$					
298.15	52.18	107.16	9.53	99.66	1.165
303.15	51.78	110.11	9.59	100.20	0.729

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308.15	50.21	114.22	9.65	101.66	0.572
$m_{D(-)fructose}=0.4 \text{ mol kg}^{-1}$					
298.15	54.21	100.79	9.52	93.73	1.478
303.15	52.91	105.10	9.55	95.64	1.261
308.15	51.12	108.26	9.58	97.43	1.173
$m_{D(-)fructose}=0.6 \text{ mol kg}^{-1}$					
298.15	56.23	99.41	9.45	92.45	1.659
303.15	55.29	103.39	9.49	95.12	1.392
308.15	52.98	107.93	9.54	97.43	1.281
$m_{D(+)galactose}=0.2 \text{ mol kg}^{-1}$					
298.15	50.24	108.35	9.61	100.77	1.086
303.15	48.36	111.27	9.63	101.26	0.695
308.15	46.91	115.92	9.66	104.33	0.425
$m_{D(+)galactose}=0.4 \text{ mol kg}^{-1}$					
298.15	51.22	105.54	9.56	98.15	1.321
303.15	50.53	107.03	9.60	98.47	1.053
308.15	49.62	113.25	9.62	101.93	0.915
$m_{D(+)galactose}=0.6 \text{ mol kg}^{-1}$					
298.15	50.45	104.18	9.50	96.89	1.114
303.15	49.28	106.34	9.57	97.83	0.992
308.15	48.38	111.05	9.69	99.95	0.711

Table.5. The values of coefficients in Eq.(11) A_0 , A_1 and A_2 at different solvent compositions.

Conc. (M)	$A_0 \cdot 10^{-6} (\text{J mol}^{-1})$	$A_1 (\text{KJ mol}^{-1}\text{K}^{-1})$	$A_2 (\text{J mol}^{-1} \text{K}^{-2})$
D(-)fructose			
0.2	-2.18	11.31	-18.82
0.4	-1.46	10.91	-18.15
0.6	-1.14	9.97	-16.60
D(-)galactose			
0.2	-2.02	10.28	-17.08
0.4	-1.35	8.49	-14.12
0.6	-1.05	8.09	-13.47

Table.6. Thermodynamic functions (ΔG_A^0 , ΔS_A^0 , ΔH_A^0) of IL in aqueous D(-)fructose and D(+)galactose solutions as a function of ionic liquid molality (m) at different temperatures.

T (K)	$\Delta G_A^0 (\text{kJ mol}^{-1})$	$\Delta S_A^0 (\text{J mol}^{-1}\text{K}^{-1})$	$\Delta H_A^0 (\text{kJ mol}^{-1})$
$m_{D(-)fructose}=0.2 \text{ mol kg}^{-1}$			
298.15	-9.59	263.30	68.91
303.15	-10.55	131.65	29.36
308.15	-10.58	11.31	-7.09
$m_{D(-)fructose}=0.4 \text{ mol kg}^{-1}$			
298.15	-9.76	253.90	65.76
303.15	-10.70	126.95	27.78
308.15	-10.75	10.91	-7.39
$m_{D(-)fructose}=0.6 \text{ mol kg}^{-1}$			
298.15	-9.92	232.33	59.35
303.15	-10.82	116.15	24.39

308.15	-10.90	9.97	-7.83
$m_{D(+)\text{galactose}} = 0.2 \text{ mol kg}^{-1}$			
298.15	-9.92	238.80	61.28
303.15	-10.64	119.40	25.56
308.15	-10.68	10.28	-7.51
$m_{D(+)\text{galactose}} = 0.4 \text{ mol kg}^{-1}$			
298.15	-10.01	197.50	48.87
303.15	-10.76	98.75	19.18
308.15	-10.81	8.49	-8.19
$m_{D(+)\text{galactose}} = 0.6 \text{ mol kg}^{-1}$			
298.15	-10.14	188.50	46.06
303.15	-10.89	94.25	17.68
308.15	-10.92	8.09	-8.43

3.4. Apparent Molar Volume

From density measurement it is shown that the densities of the IL in each aqueous D(-)fructose and D(+)-galactose increase linearly with the concentration at the studied temperatures. The density values of IL are higher in aqueous D(-)fructose solution than in aqueous D(+)-galactose solution. For this purpose, the apparent molar volumes ϕ_V were determined from the solution densities using the following equation

$$\phi_V = M / \rho - (\rho - \rho_o) / m \rho_o \rho \quad (14)$$

Where M is the molar mass of the solute, m is the molality of the solution, ρ and ρ_o are the densities of the solution and solvent, respectively.

The limiting apparent molar volumes ϕ_V^0 were calculated using a least-squares treatment to the plots of ϕ_V versus \sqrt{m} using the following Masson equation [73].

$$\phi_V = \phi_V^0 + S_V^* \cdot \sqrt{m} \quad (15)$$

Where, ϕ_V^0 is the limiting apparent molar volume at infinite dilution and S_V^* is the experimental slope.

The limiting apparent molar volumes ϕ_V^0 are found to increase with increasing molality (m) of IL in each solvents and decrease with increasing temperature for the studied system. From Table. 7 it is observed that ϕ_V^0 values are positive in both the solution systems and is higher in case of D(-)fructose

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compared to D(+)galactose. This indicates the presence of strong ion–solvent interactions and the extent of interactions increases in D(-)fructose than in D(+)galactose solution (Fig. 4). On the contrary, the S_V^* indicates the extent of ion-ion interaction. The values of S_V^* shows that the extent of ion-ion interaction is higher in case of D(+)galactose than D(-)fructose. Owing to a quantitative comparison, the magnitude of ϕ_V^0 are much greater than S_V^* , in every solutions, suggests that ion-solvent interactions dominate over ion-ion interactions in all the solutions. The values of ϕ_V^0 also support the fact that higher ion-solvent interaction of IL leads to lower conductance in D(-)fructose than D(+)galactose, discussed earlier [217] [218].

The transfer volumes, $\Delta_r\phi_V^0$ of D(-)fructose and D(+)galactose from water to aqueous [bmpy]Cl solutions have been calculated as follows [219]-

$$\Delta_r\phi_V^0 = \phi_V^0(\text{in [bmp]Cl + aq carbohydrate}) - \phi_V^0(\text{aq.}) \quad (16)$$

Where $\phi_V^0(\text{in [bmp]Cl + aq carbohydrate})$ and $\phi_V^0(\text{aq.})$ are the standard partial molar volumes of [bmp]Cl in aqueous carbohydrates [D(-)fructose and D(+)galactose] and in water, respectively. The obtained values for the transfer volumes are given in Table. 8. Here we have determined the standard partial molar volume of aqueous carbohydrates. **Table.8.** shows, the values of $\Delta_r\phi_V^0$ values are positive and increase with increase in the concentration of ionic liquid at each experimental temperatures. The following types of interactions are possible between solute [D(-)fructose and D(+)galactose] and co-solute (ionic liquid) in ternary solutions : (i) Hydrophilic–ionic interactions between the hydrophilic sites (-OH, -C=O, and -O-) of [D(-)fructose and D(+)galactose] and the ions [bmp]⁺Cl⁻ of ionic liquid; (ii) Hydrophobic–ionic interactions between the hydrophobic parts of [D(-)fructose and D(+)galactose] and the ions of ionic liquid. According to the co-sphere overlap model [220], the positive $\Delta_r\phi_V^0$ values obtained for D(-)fructose and D(+)galactose in the studied solutions suggest that the hydrophilic–ionic interactions predominate over the hydrophobic–ionic interactions.

Thus the interactions between IL and carbohydrate in aqueous medium can generally be summarized as, (a) the hydrogen bonding interaction between the H atoms of water with (i) -O atom of the –OH group attached to the carbohydrate and (ii) –N atom in the heterocyclic ring of IL; (b) the hydrogen bonding interaction between the O atom of water with the H atom associated with the –OH group attached to the carbohydrate. Therefore, more the number of interacting centres (–OH group) present in the carbohydrate, more is its interaction with the IL. A possible interaction between the plausible products (obtained with reaction between different carbohydrates and IL) with water is given in **Scheme1.**

Interaction pattern between D(-)fructose, D(+)galactose and IL can be summarized as [219] -

- The hydrophilic-ionic interactions between the –OH group of the saccharides and the ionic part of IL.
- The hydrophilic-hydrophilic interactions occurring between the –OH group of the saccharides and N-atom of pyrrolidinium group present in IL.
- The hydrophilic-hydrophobic interactions present between the –OH group of the saccharides and the non-polar part of the IL.

The overall positive values of ϕ_v^0 (**Table.7.**) for the systems reinforce the fact that the solute-solvent interactions are predominate. Therefore the mutual overlap of the hydration spheres of solute and co-solute molecules will lead to an increase in the magnitude of hydrogen bonding interactions between the plausible products (obtained with reaction between IL and different carbohydrates) with water. The observation shows that with increase in the number of the interacting centers (-OH groups) present in the studied carbohydrates, the solute-solvent interaction also increases[221] [222] [223]. The solute-solvent interaction in case of D(-)fructose is greater than D(+)galactose because of the presence of greater number of free –OH group in D(-)fructose. Also D(+)galactose is six-membered ring so there is some sort of structural restriction, whereas D(-)fructose is five-membered ring which containing more free –OH group favored H-bonding to a greater extent. Therefore, the solute-solvent interaction is superior in D(-)fructose compared to D(+)galactose solution.

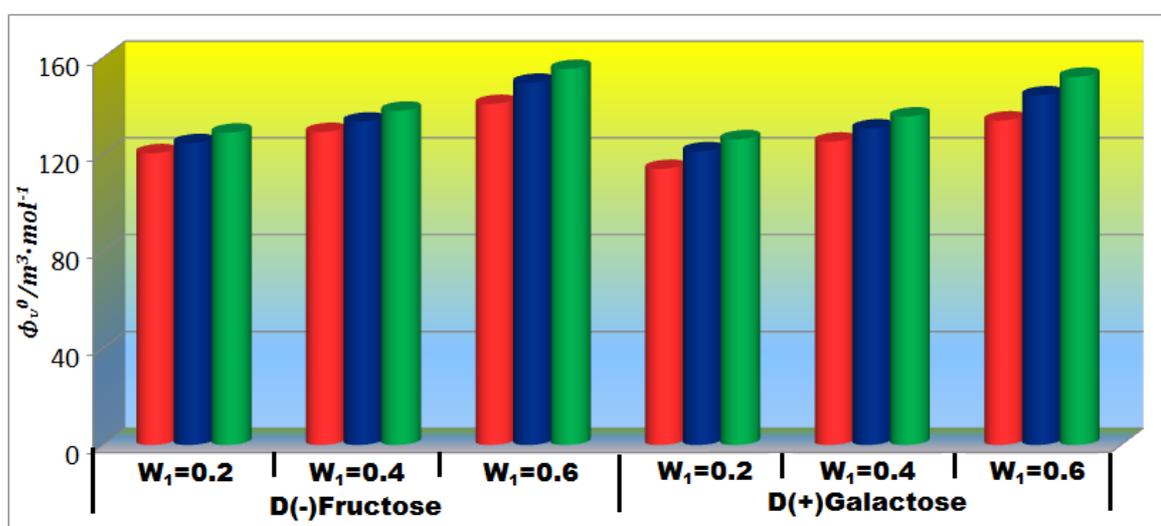


Fig.4. Plot of limiting molar volume (ϕ_v^0) of IL against mass fraction (w) of aqueous D(-)fructose and D(+)galactose at 298.15K (red), 303.15K (blue) and 308.15K (green) respectively.

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Table.7. Limiting apparent molar volume (ϕ_V^0), experimental slope (S_V^*), viscosity-B and A coefficients of IL in aqueous D(-)fructose and D(+)galactose solutions at different temperatures.

T (K)	$\phi_V^0 \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	$S_V^* \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-3/2} \cdot \text{dm}^{3/2}$	$B / \text{dm}^3 \cdot \text{mol}^{-1}$	$A / \text{dm}^{3/2} \cdot \text{mol}^{-1/2}$
$m_{\text{D(-)fructose}} = 0.2 \text{ mol kg}^{-1}$				
298.15	120.56	-242.28	0.959	-0.0749
303.15	129.31	-259.39	1.108	-0.0780
308.15	140.91	-337.66	1.213	-0.0851
$m_{\text{D(-)fructose}} = 0.4 \text{ mol kg}^{-1}$				
298.15	124.73	-237.81	1.159	-0.0779
303.15	133.62	-249.15	1.301	-0.0868
308.15	149.67	-329.07	1.376	-0.0951
$m_{\text{D(-)fructose}} = 0.6 \text{ mol kg}^{-1}$				
298.15	129.03	-233.04	1.457	-0.0959
303.15	138.12	-246.93	1.529	-0.0967
308.15	155.35	-321.23	1.662	-0.0979
$m_{\text{D(+)galactose}} = 0.2 \text{ mol kg}^{-1}$				
298.15	114.05	-256.05	0.907	-0.0602
303.15	125.35	-269.07	1.088	-0.0685
308.15	134.08	-338.68	1.185	-0.0712
$m_{\text{D(+)galactose}} = 0.4 \text{ mol kg}^{-1}$				
298.15	121.38	-240.15	1.136	-0.0670
303.15	130.77	-257.67	1.273	-0.0794
308.15	144.43	-336.45	1.313	-0.0856
$m_{\text{D(+)galactose}} = 0.6 \text{ mol kg}^{-1}$				
298.15	126.29	-235.65	1.316	-0.0747
303.15	135.72	-248.21	1.356	-0.0790
308.15	152.16	-324.43	1.462	-0.0841

Table.8. Values of $\phi_V^0(\text{aq})$, $\Delta\phi_{V_{\text{tr}}}^0$, $B(\text{aqueous})$, ΔB for IL in different solvent systems at different temperatures.

Temp /K	$\phi_V^0 \cdot 10^6 (\text{aq}) / \text{m}^3 \cdot \text{mol}^{-1}$	$\Delta\phi_{V_{\text{tr}}}^0 \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	$B(\text{aq}) / \text{kg} \cdot \text{mol}^{-1}$	$\Delta B / \text{kg} \cdot \text{mol}^{-1}$
$m_{\text{D(-)fructose}} = 0.2 \text{ mol kg}^{-1}$				
298.15	112.01	8.55	0.890	0.069
303.15	112.23	17.08	1.033	0.075
308.15	112.71	28.20	1.129	0.084
$m_{\text{D(-)fructose}} = 0.4 \text{ mol kg}^{-1}$				
298.15	112.95	11.78	1.085	0.074
303.15	113.03	20.59	1.22	0.081
308.15	113.11	36.56	1.283	0.093
$m_{\text{D(-)fructose}} = 0.6 \text{ mol kg}^{-1}$				
298.15	113.21	15.82	1.377	0.080
303.15	113.27	24.85	1.44	0.089
308.15	113.35	42.00	1.563	0.099
$m_{\text{D(+)galactose}} = 0.2 \text{ mol kg}^{-1}$				
298.15	112.01	2.04	0.842	0.065
303.15	112.23	13.12	1.016	0.072

308.15	112.71	21.37	1.102	0.083
$m_{D(+)\text{galactose}} = 0.4 \text{ mol kg}^{-1}$				
298.15	112.95	8.43	1.065	0.071
303.15	113.03	17.74	1.197	0.076
308.15	113.11	31.32	1.234	0.079
$m_{D(+)\text{galactose}} = 0.6 \text{ mol kg}^{-1}$				
298.15	113.21	13.08	1.242	0.074
303.15	113.27	22.45	1.275	0.081
308.15	113.35	38.81	1.369	0.093

3.5. Temperature dependent limiting apparent molar volume

The temperature dependent general polynomial equation for ϕ_V^0 are as follows [224]

$$\phi_V^0 = a_0 + a_1T + a_2T^2 \quad (17)$$

Where, a_0 , a_1 , a_2 are the empirical and T is the Kelvin temperature. The values of these coefficients are presented in **Table.9**. The limiting apparent molar expansibilities, ϕ_E^0 , can be obtained by the following equation,

$$\phi_E^0 = \left(\delta \phi_V^0 / \delta T \right)_P = a_1 + 2a_2T \quad (18)$$

Where, ϕ_E^0 is the change in magnitude with the change of temperature at constant pressure. The values of ϕ_E^0 for different solutions of the studied ILs at different Kelvin are reported in **Table.10**. Positive values of ϕ_E^0 obtained can be ascribed to the absence of caging or packing effect for the IL in solutions.

Hepler [225] developed a technique of examining the sign of $(\delta \phi_E^0 / \delta T)_P$ for the solute in terms of long-range structure-making and breaking capacity of the solute in the mixed solvent systems using the general thermodynamic expression,

$$\left(\delta \phi_E^0 / \delta T \right)_P = \left(\delta^2 \phi_V^0 / \delta T^2 \right)_P = 2a_2 \quad (19)$$

If the sign of $(\delta \phi_E^0 / \delta T)_P$ becomes positive or a small negative, the molecule is a structure maker; otherwise, it is a structure breaker [226]. From **Table.10**, the $(\delta \phi_E^0 / \delta T)_P$ values are found to be positive for the IL in both the solution of D(-)fructose and D(+)-galactose [in 0.2 (m) D-galactose solution small negative] and this implies that the IL is structure maker in all of the experimental solutions for D(-)fructose and D(+)-galactose in aqueous medium and saccharides behave as a structure breaker in aqueous system. Since with increasing temperatures, some slackly leaped carbohydrate molecules are released from the secondary solvation shells of the ions, so the solute-solvent interactions can become stronger with the increase of temperature [227].

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Table.9. Values of empirical coefficients (a_0 , a_1 , and a_2) of eqn (17) for IL in different solvent systems.

Conc. (m)	$a_0 \cdot 10^{-6}$ (J mol ⁻¹)	a_1 (KJ mol ⁻¹ K ⁻¹)	a_2 (J mol ⁻¹ K ⁻²)
D(-)fructose			
0.2	0.0085	-0.0569	0.0097
0.4	0.0125	-0.0843	0.1432
0.6	0.0143	-0.0967	0.1628
D(+)galactose			
0.2	-0.0052	0.0332	-0.0510
0.4	0.0153	-0.1027	0.1734
0.6	0.0195	-0.1309	0.2202

Table.10. Limiting apparent molal expansibilities (ϕ_E^0) and $(\delta\phi_E^0/\delta T)_P$ for IL in different solvent systems at different temperatures.

T (K)	ϕ_E^0	$(\delta\phi_E^0/\delta T)_P$
$m_{D(-)fructose}=0.2 \text{ mol kg}^{-1}$		
298.15	57.78	0.194
303.15	58.75	0.194
308.15	59.72	0.194
$m_{D(-)fructose}=0.4 \text{ mol kg}^{-1}$		
298.15	85.30	0.286
303.15	86.61	0.286
308.15	88.04	0.286
$m_{D(-)fructose}=0.6 \text{ mol kg}^{-1}$		
298.15	100.20	0.336
303.15	101.76	0.336
308.15	103.44	0.336
$m_{D(+)}galactose=0.2 \text{ mol kg}^{-1}$		
298.15	-29.84	-0.100
303.15	-30.04	-0.100
308.15	-30.84	-0.100
$m_{D(+)}galactose=0.4 \text{ mol kg}^{-1}$		
298.15	103.29	0.347
303.15	105.02	0.347
308.15	106.76	0.347
$m_{D(+)}galactose=0.6 \text{ mol kg}^{-1}$		
298.15	129.99	0.440
303.15	133.37	0.440
308.15	135.57	0.440

3.5. Viscosity calculation

The viscosity data have been analysed using Jones-Dole equation [75]

$$(\eta/\eta_0 - 1)/\sqrt{c} = A + B\sqrt{m} \quad (20)$$

Where, η and η_0 are the viscosities of the solution and solvent respectively. The viscosity co-efficient A - and B - represent ion-ion and ion-solvent interaction respectively. The positive values of B -coefficients indicate greater ion-solvent interactions and small negative values of A - coefficients

indicate smaller ion-ion interaction in solution (**Table.7**). The B -coefficient [228] value obtained from the viscosity measurements gives the important information regarding the extent of solvation of the solute molecules and the effects on the structure of the solvents in the local vicinity of the solute molecule in solution. The higher B -coefficient values are due to the solvated solutes molecule associated by the solvent molecules by solute-solvent interactions. These types of interactions are strengthened with rise in temperature and thus the values of B -coefficient increases with increase in temperature. As a consequence, the inclination of ion-solvent interaction is higher in case of D(-)fructose solution than in D(+)galactose solution (**Fig.5**). These results are in good agreement with those obtained from ϕ_V^0 and S_V^* values, discussed earlier.

Viscosity B -coefficients of transfer (ΔB) from water to different aqueous carbohydrate solutions have been determined using the relations [229] [230]

$$\Delta B(IL) = B(IL + aq. carbohydrate) - B(aq.) \quad (21)$$

From **Table.8**, it is evident that ΔB values are positive and increases with a rise in temperature and with increasing concentration of carbohydrate and it suggests the presence of strong solute-solvent interactions, and the interactions are strengthened with rise in temperature and increase of carbohydrate in aqueous mixture [231]. The observation supports the same results obtained from $\Delta_r \phi_V^0$ values discussed above.

The sign of dB/dT decides structure-forming or -breaking ability of the solute [225]. It is found from **Table.11**, that the values of the B -coefficient increase with a rise in temperature (positive dB/dT values), suggesting the structure breaking tendency [220] of carbohydrates in the solution systems. Moreover, it is interesting to note that the B -coefficients of the studied carbohydrates show a linear relationship with the partial molar volumes ϕ_V^0 , i.e.

$$B = A_1 + A_2 \phi_V^0 \quad (22)$$

The coefficients A_1 and A_2 are included in **Table.11**. The positive slope (or A_2) shows the linear variation of B -coefficient with partial molar volumes ϕ_V^0 . This relationship is really expected, since both the viscosity B -coefficient and the partial molar volume reflect the privileged solute-solvent interactions in the solutions.

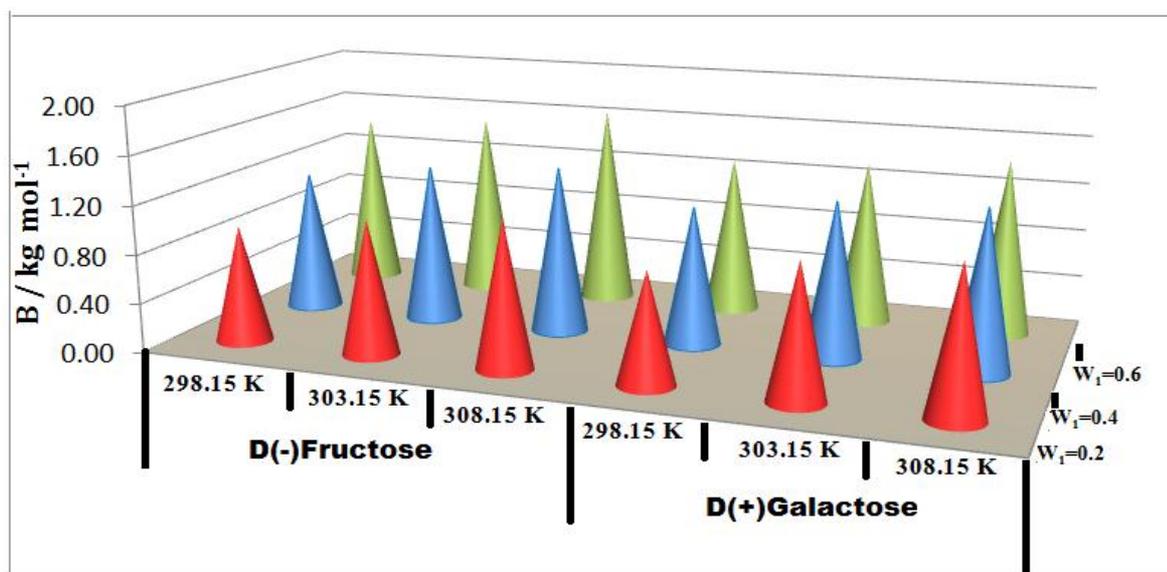


Fig.5. Plot of viscosity B -coefficient of IL against mass fraction (w) of aqueous D(-)fructose and D(+)galactose at different temperatures

Table.11. Values of dB/dT , A_1 and A_2 coefficient of equation (22) for the IL in different solvent systems.

Conc. (m)	dB/dT	A_1	A_2
IL+aqueous D(-)fructose			
0.2	0.0071	-0.508	0.012
0.4	0.0076	0.161	0.008
0.6	0.0081	0.453	0.007
IL+aqueous D(+)galactose			
0.2	0.0068	-0.480	0.014
0.4	0.0074	0.271	0.007
0.6	0.0077	0.586	0.005

3. ^1H NMR study

NMR study is one of the most imperative spectroscopic tools for understanding the microscopic information about the ion-solvent interaction of the IL in carbohydrate solution systems. In our present work, we have considered the interactions of an IL (*viz.*, [bmp]Cl) with D(-)fructose and D(+)galactose by ^1H NMR study taking 1:1 molar ratio of IL and CD in D_2O at 298.15K [Fig. 6(a) and 6(b)]. ^1H NMR data of the IL, two carbohydrates and mixture of IL-Carbohydrates are listed in **Table.12**. The protons of the IL show considerable chemical shift due to the interaction with the hydrophilic $-\text{OH}$ groups present in the carbohydrate molecules. In the structure of D(-)Fructose the H1-H6 i.e. all the H-atoms situated in the moiety show the peak in NMR study. Similarly in case of D(+)Galactose the H1-H6 i.e. all the H-atoms situated in the carbohydrate moiety show the peak in NMR study. The chemical shifts for H-atoms of IL evidently show highfield in presence carbohydrates [232]. It can be concluded that the interactions between the IL and carbohydrates would be mainly resolute by their

dehydrations/hydrations in the processes. The change of chemical shift may be due to the disruption of the interionic hydrogen bonding network in ILs [233]. In case of mixture compositions, the variations of relative chemical shifts in thus commenced are interpreted in terms of specific and non-specific intermolecular interactions [234]. The results showed that the solvation process of carbohydrates is governed mainly by the interactions between the cationic part of the IL and carbohydrate molecules. The shifts of protons of IL are more in case D(-)fructose than that of D(+)galactose. The NMR study provides a profound insight into other IL + biomolecule mixed systems, especially gives imperative information for studies on the potential toxicity of ILs.

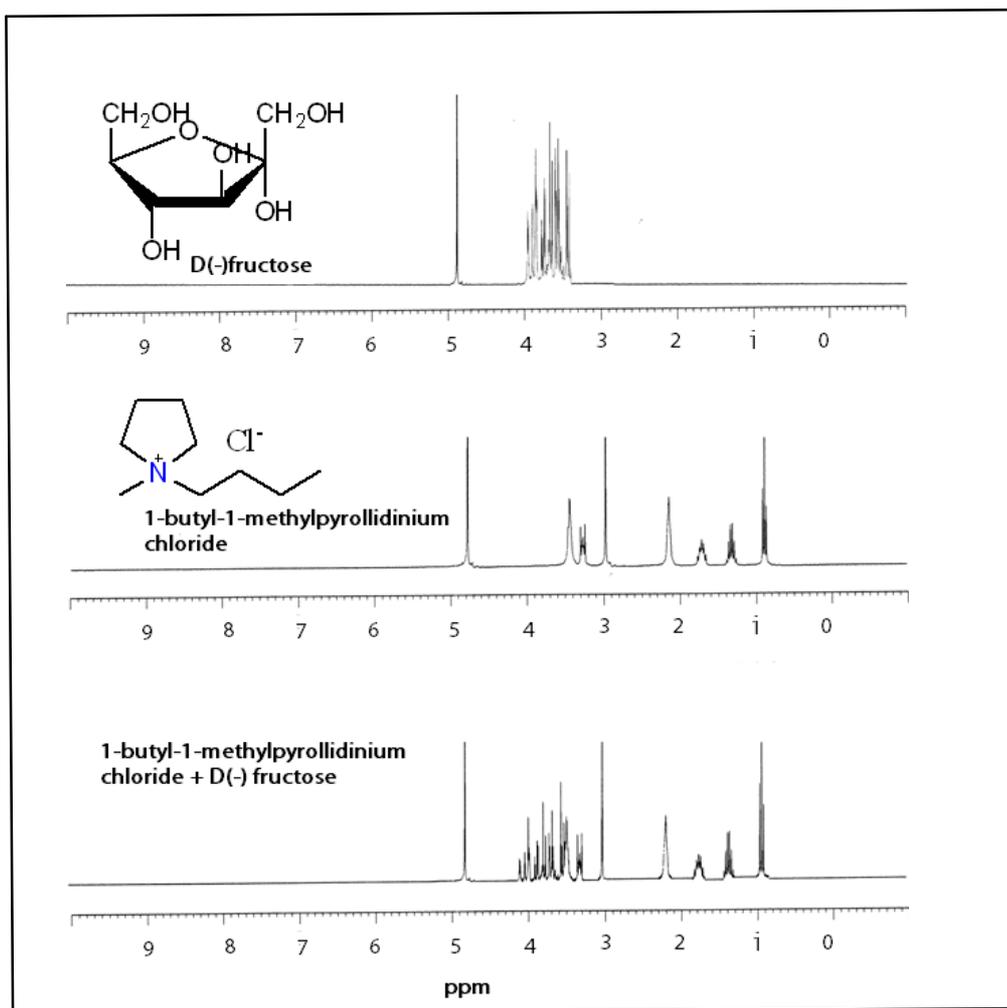


Fig.6(a). ¹H NMR Spectra of D(-)Fructose, [bmp]Cl and 1:1 molar ratio of D(-)Fructose + [bmp]Cl in D₂O in 298.15 K.

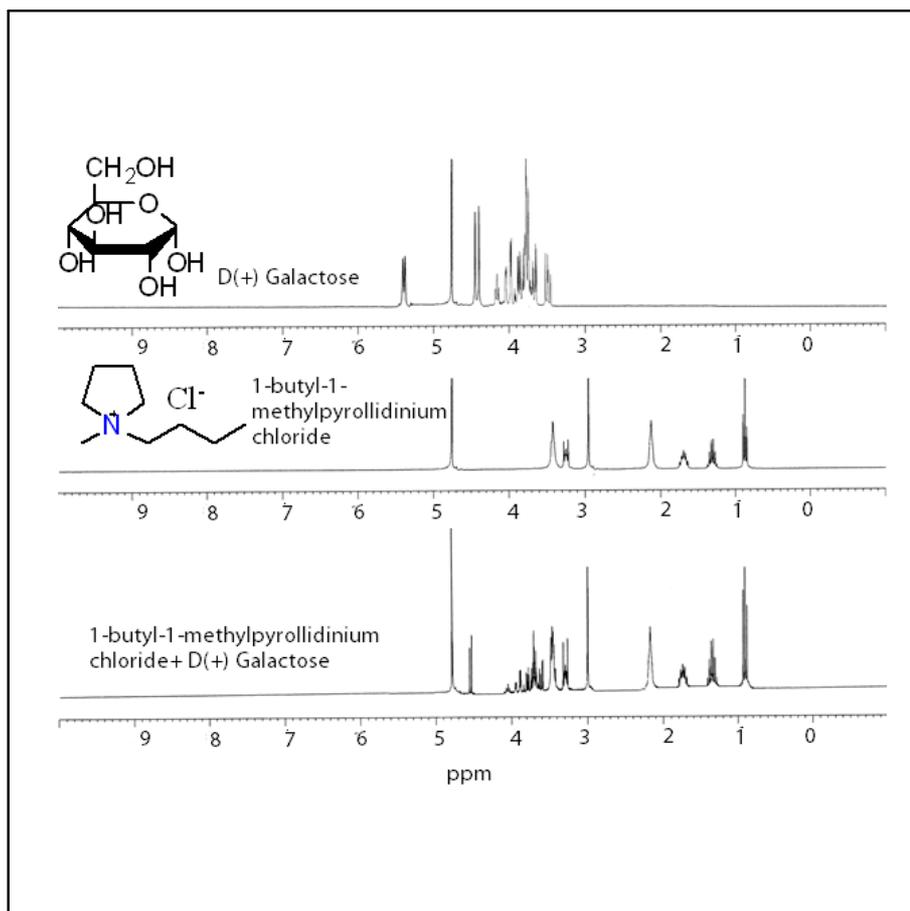


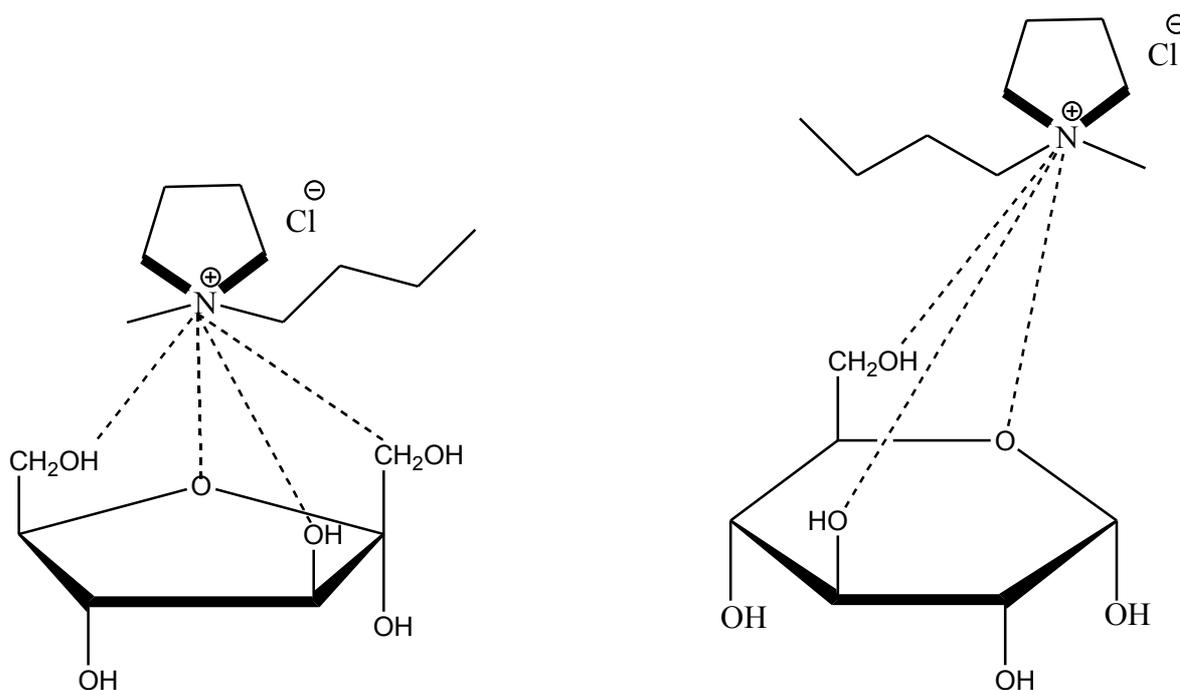
Fig. 6(b). ^1H NMR Spectra of D(+)-Galactose, [bmp]Cl and 1:1 molar ratio of D(+)-Galactose + [bmp]Cl in D_2O in 298.15 K.

Table.12. ^1H NMR data of [bmp]Cl, D(-)-fructose, D(+)-galactose and IL- carbohydrates mixture.

[bmp]Cl (300MHz, Solv: D_2O) δ /ppm	
0.91-0.96 (3H, t, $J = 7.29$ Hz), 1.34-1.41 (2H, m), 1.74-1.81(2H,m), 2.19 (4H, m), 3.02 (3H, s), 3.28-3.34 (2H, m), 3.48 (4H, m)	
D(-)-fructose (300 MHz, Solv: D_2O) δ /ppm	D(+)-galactose (300 MHz, Solv: D_2O) δ /ppm
3.49-3.53 (2H, d), 3.64-3.68 (1H, m), 3.69-3.73 (1H, m), 3.77-3.84 (1H, m), 3.88-3.95 (1H, m), 3.94-4.06 (2H, d)	3.42-3.47 (2H, d), 3.58-3.61 (1H, m), 3.63-3.70 (1H, m), 3.72-3.79 (1H, m), 3.88-3.94 (1H, m), 4.53-4.55 (1H, d)
[bmp]Cl in D(-)-fructose (1:1 molar ratio, 300 MHz, Solv: D_2O) δ /ppm	[bmp]Cl in D(+)-galactose (1:1 molar ratio, 300 MHz, Solv: D_2O) δ /ppm
0.87-0.92 (3H, t), 1.28-1.31 (2H, m), 1.72-1.80 (2H, m), 2.11-2.15 (4H, m), 2.98 (3H, s), 3.20-3.31 (2H, m), 3.40-3.46 (1H, m), 3.45-3.48 (2H, d), 3.59-3.65 (1H, m), 3.67-3.70 (1H, m), 3.71-3.79 (1H, m), 3.81-3.90 (1H, m), 3.91-4.01 (2H, d)	0.90-0.95 (3H, t), 1.29-1.39 (2H, m), 1.73-1.81 (2H, m), 2.14-2.18 (4H, m), 3.00 (3H, s), 3.24-3.32 (2H, m), 3.46-3.48 (4H, m), 3.41-3.45 (2H, d), 3.56-3.60 (1H, m), 3.60-3.67 (1H, m), 3.69-3.76 (1H, m), 3.84-3.92 (1H, m), 4.51-4.53 (1H, d)

4. CONCLUSION

In our present work, we have focused on the characteristic interfaces of some model biological systems [D(-)fructose and D(+)galactose], with an IL. From the analysis of thermodynamic data, it is revealed that the association process for [bmp]Cl is higher in case of D(+)galactose than in D(-)fructose solution and is endothermic and controlled by entropy at all temperatures. Density and viscosity studies interpret limiting apparent molar volume, ϕ_v^0 and viscosity B -coefficient is increased with increasing the conc. of D(-)fructose and D(+)galactose and decreased with increasing temperature. NMR study analysis reveals that no specific and stronger interactions occur between IL and carbohydrates. However the study confirms that interaction of IL with carbohydrates is higher in D(-)fructose than that of D(+)galactose.



Interaction between D(-)fructose and IL (I₁) Interaction between D(+)galactose and IL (I₂)

I₁>I₂

Scheme1: Plausible Interfaces between ionic liquid and diverse solvent systems

