CHAPTER IX

Solution properties and taste behavior of lactose monohydrate in aqueous L-ascorbic acid solutions at different temperatures: Volumetric and rheological approach[*]

9.1. Introduction

Lactose is a milk sugar composed of one galactose and one glucose molecule. It has significant role in the biological and food industrial processes [1]. Food producers use lactose as filler in bread. As lactose does not have any flavor so using lactose in food does not change its flavor. In food industries it is used as an alternative sweetener. Additionally, as lactose can help to prevent food discoloration it can be used in canned and frozen vegetables. Most of the powdered food products such as soups, meal-replacement supplements and dehydrated potatoes generally contain lactose. Further some non-dairy foods like coffee creamers contain lactose in the state of dry milk solids or whey. In the pharmaceutical industry, lactose is used as a coating or filler in many prescription and over-the-counter drugs including birth control pills, antacids, vitamin pills and throat lozenges because of its excellent compressibility properties [2, 3]. However major problem with the diary product is their short shelf life, *i.e.*, they get expired over a short period of time. To get rid of this problem food additives are often used. Substances added for the preservation of food and to enhance its appearance and taste quality are generally known as food additives. Ascorbic acid commonly known as vitamin-C is used as antioxidant food additive [4]. It is mainly applied to food and feed to increase product stability and quality. So L-ascorbic acid is added to foodstuffs to retain its characteristic aroma, nutrients and other properties during processing or before packing. It is also essential for growth, healthy teeth, gums, bones, skin and blood vessels and aiding the absorption of iron [5].

Volumetric studies provide information regarding solute-solvent interactions and related structural changes affect the apparent molar volume, which in turn produces corresponding changes in the taste behavior of a solute [1]. Apparent specific volume is a parameter with great importance to foods as it gives a clear idea about the taste chemoreception mechanism [6]. The determination of the viscosity data can be used to study the structural property and the solvation of the solute, which

in turn determines the stability of the solute in the solution [7]. Although a number of experiments have been made to explain the properties of lactose and L-ascorbic acid but such a study on the solution properties and taste behavior of lactose monohydrate in aqueous L-ascorbic acid solutions is not available in the literature [8-13]. So in this chapter the an attempt has been undertaken to reveal the effect of L-ascorbic acid on the volumetric, rheological and taste properties of lactose monohydrate in aqueous solutions at temperatures from 298.15 to 318.15 K. The results have been interpreted in terms of solute-cosolute and solute-solvent interactions in terms of apparent molar volumes, standard partial molar volumes and viscosity B-coefficients and an attempt has been made to study the effect of L-ascorbic acid on the taste behavior of lactose monohydrate.

## 9.2. Experimental Section

9.2.1. Chemicals used

Reagent grade lactose monohydrate (CAS: 64044-51-5; Sigma-Aldrich, mass fraction purity > 0.980) and A. R grade L-ascorbic acid (CAS: 50-81-7, Sigma-Aldrich, mass fraction purity > 0.990) were used for present study. Provenance and purity of the chemicals used is given in chapter III. The chemicals were used as such but stored in *vacuo* over anhydrous $CaCl_2$ for several hours before use. Doubly distilled de-ionized water with a specific conductance $< 1 \cdot 10^{-6}$ S$\cdot$cm^{-1} at 298.15 K was used to prepare different aqueous solutions of L-ascorbic acid. Various mixed solvents were prepared by mass and necessary adjustments were done to achieve exact molal concentrations ($m = 0.02$, 0.04, 0.06 and 0.08 mol.kg^{-1}) of L-ascorbic acid in the mixed solvents. The physical properties of these mixed solvents are given in Table 9.1. Stock solutions of lactose monohydrate in different solvent mixtures were prepared by mass (measured by Mettler, AG 285, Switzerland) and all the experimental solutions were prepared afresh before use by mass dilution and uncertainty in mass measurements was $\pm 1 \cdot 10^{-4}$ g. Molalities were converted into molarities by using experimental density data [14]. Uncertainty in molalities of lactose monohydrate in the studied solutions was estimated to be within $\pm 1 \cdot 10^{-4}$ mol.kg^{-1}.

Table 9.1. Densities (ρ) and viscosities (η) of different aqueous solutions of L-ascorbic acid at $T = (298.15 \text{ to } 318.15)$ K.

m^a	T/K	$\dfrac{\rho \times 10^{-3}}{(\text{kg} \cdot \text{m}^{-3})}$	$\dfrac{\eta}{(\text{mPa} \cdot \text{s})}$
	298.15	0.99840	0.8981
0.02	308.15	0.99534	0.7237
	318.15	0.99153	0.6006
	298.15	0.99971	0.9053
0.04	308.15	0.99662	0.7293
	318.15	0.99281	0.6051
	298.15	1.00103	0.9124
0.06	308.15	0.99790	0.7350
	318.15	0.99409	0.6097
	298.15	1.00235	0.9196
0.08	308.15	0.99918	0.7406
	318.15	0.99537	0.6142

[a] molality of L-ascorbic acid in mol kg^{-1}.
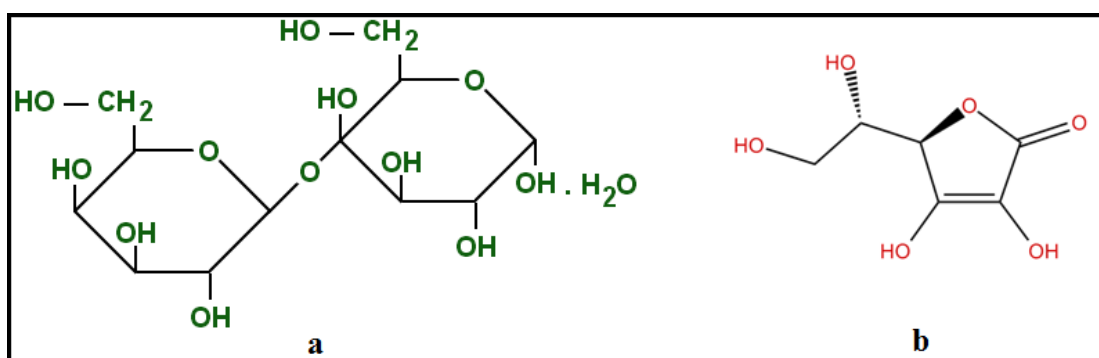
9.1. Molecular structures of (a) lactose monohydrate and (b) L-ascorbic acid.

Chapter IX

9.2.2 Apparatus and procedure

Densities were measured by means of a vibrating-tube densimeter (DMA 4500 M, Anton Paar). Viscosities were measured with the help of an Ubbelohde type capillary viscometer thoroughly cleaned and dried. The detail procedure of density and viscosity measurements are already given in chapter IV.

The absorption spectra of lactose monohydrate in aqueous l-ascporbic acid solutions were recorded on Jasco V-530 double beam UV-VIS Spectrophotometer coupled with thermostatic arrangement and maintained at 298.15 K. A quartz cell of 1 cm path length was used for holding the experimental solutions. Spectroscopic grade water was used as the reference solvent for all the absorption measurements. During spectrophotometric measurements, 2 mL of either lactose monohydrate or l-ascporbic acid solution $(1 \cdot 10^{-4} \, \text{mol L}^{-1})$ was placed in the quartz cell and the absorbance of the solution was measured. Then 40 µL of either L-ascorbic acid $(1 \cdot 10^{-4} \, \text{mol L}^{-1})$ or lactose monohydrate $(1 \cdot 10^{-4} \, \text{mol L}^{-1})$ solution was added in a stepwise fashion through a micropipette. The absorbance of the experimental solution was measured at each step. A Systronics digital pH meter, calibrated at pH = 4.00, was used to measure pH of the aqueous L-ascorbic acid solutions at 298.15 K. pH's were 3.12, 3.00, 2.92 and 2.86, respectively for (0.02, 0.04, 0.06 and 0.08 mol kg^{-1}) aqueous solutions of L-ascorbic acid.

9.3. Results and discussion

The experimental molalities m, densities (ρ), viscosities (η), and apparent molar volumes (ϕ_V) of lactose monohydrate in various aqueous L-ascorbic acid solutions (used as solvents) at the experimental temperatures are reported in Supplementary Table 9.2.

9.3.1. Standard partial molar volumes

The experimental determination of partial molar volume involves the careful measurement of the densities of solutions of known concentrations. The calculation is simplified by the use of a related quantity called apparent molar volume (ϕ_V), which is the volume due to added solute per mole in the solution [16].

Chapter IX

Table 9.2. Molalities (m), densities (ρ), viscosities (η), apparent molar volumes (ϕ_V) and apparent specific volumes (ϕ_{Vsp}) of lactose monohydrate in aqueous solutions of L-ascorbic acid at $T = (298.15$ to $318.15)$ K.

$\dfrac{m^a}{(\text{mol}\cdot\text{kg}^{-1})}$	$\dfrac{\rho\cdot10^{-3}}{(\text{kg}\cdot\text{m}^{-3})}$	$\dfrac{\eta}{(\text{mPa}\cdot\text{s})}$	$\dfrac{\phi_V\cdot10^6}{(\text{m}^3\cdot\text{mol}^{-1})}$	$\dfrac{\phi_{Vsp}\cdot10^6}{(\text{m}^3\cdot\text{kg}^{-1})}$
0.00 mol kg^{-1} aqueous L-ascorbic acid solution				
$T/\text{K} = 298.15$				
0.0202	0.99974	0.9132	227.40	0.63
0.0366	1.00189	0.9311	227.52	0.63
0.0532	1.00403	0.9490	227.71	0.63
0.0699	1.00620	0.9680	227.75	0.63
0.0869	1.00837	0.9872	227.87	0.63
0.1041	1.01054	1.0064	227.91	0.63
$T/\text{K} = 308.15$				
0.0202	0.99671	0.7341	228.59	0.63
0.0366	0.99885	0.7460	228.70	0.63
0.0532	1.00098	0.7591	228.82	0.63
0.0699	1.00313	0.7711	228.92	0.63
0.0869	1.00529	0.7843	228.98	0.63
0.1041	1.00744	0.7964	229.09	0.64
$T/\text{K} = 318.15$				
0.0202	0.99289	0.6041	229.92	0.64
0.0366	0.99501	0.6101	230.01	0.64
0.0532	0.99713	0.6161	230.11	0.64
0.0699	0.99927	0.6232	230.18	0.64
0.0869	1.00141	0.6292	230.26	0.64

Contd...

0.1041	1.00355	0.6364	230.35	0.64

<div align="center">0.02 mol kg^{-1} aqueous L-ascorbic acid solution</div>

		$T/K = 298.15$		
0.0202	1.00106	0.9201	227.78	0.63
0.0366	1.00319	0.9391	227.98	0.63
0.0532	1.00533	0.9581	228.19	0.63
0.0699	1.00747	0.9772	228.31	0.63
0.0869	1.00963	0.9964	228.41	0.63
0.1041	1.01178	1.0156	228.54	0.63
		$T/K = 308.15$		
0.0202	0.99799	0.7373	229.12	0.64
0.0366	1.00010	0.7504	229.27	0.64
0.0532	1.00223	0.7624	229.44	0.64
0.0699	1.00435	0.7767	229.62	0.64
0.0869	1.00649	0.7887	229.75	0.64
0.1041	1.00863	0.8020	229.82	0.64
		$T/K = 318.15$		
0.0202	0.99416	0.6073	230.40	0.64
0.0366	0.99626	0.6144	230.48	0.64
0.0532	0.99838	0.6204	230.58	0.64
0.0699	1.00049	0.6288	230.70	0.64
0.0869	1.00262	0.6348	230.85	0.64
0.1041	1.00475	0.6408	230.89	0.64

Contd...

0.04 mol kg⁻¹ aqueous L-ascorbic acid solution				
$T/K = 298.15$				
0.0202	1.00237	0.9258	228.00	0.63
0.0366	1.00449	0.9460	228.26	0.63
0.0532	1.00662	0.9639	228.38	0.63
0.0699	1.00875	0.9842	228.57	0.63
0.0869	1.01089	1.0033	228.68	0.63
0.1041	1.01305	1.0226	228.77	0.63
$T/K = 308.15$				
0.0202	0.99925	0.7429	229.74	0.64
0.0366	1.00135	0.7548	229.94	0.64
0.0532	1.00346	0.7668	230.06	0.64
0.0699	1.00557	0.7822	230.19	0.64
0.0869	1.00770	0.7955	230.31	0.64
0.1041	1.00982	0.8075	231.45	0.64
$T/K = 318.15$				
0.0202	0.99543	0.6139	230.92	0.64
0.0366	0.99751	0.6199	231.07	0.64
0.0532	0.99961	0.6247	231.17	0.64
0.0699	1.00171	0.633	231.29	0.64
0.0869	1.00383	0.6403	231.38	0.64
0.1041	1.00595	0.6487	231.43	0.64
0.06 mol kg⁻¹ aqueous L-ascorbic acid solution				
$T/K = 298.15$				
0.0202	1.00366	0.9327	228.76	0.63
0.0366	1.00577	0.9506	228.93	0.63
0.0532	1.00788	0.9697	229.15	0.64

Contd...

0.0699	1.01000	0.9922	229.27	0.64
0.0869	1.01213	1.0103	229.34	0.64
0.1041	1.01426	1.0295	229.47	0.64
		$T/K = 308.15$		
0.0202	1.00050	0.7473	230.67	0.64
0.0366	1.00258	0.7604	230.87	0.64
0.0532	1.00467	0.7735	230.99	0.64
0.0699	1.00677	0.7878	231.04	0.64
0.0869	1.00887	0.8010	231.17	0.64
0.1041	1.01098	0.8142	231.25	0.64
		$T/K = 318.15$		
0.0202	0.99667	0.6158	231.96	0.64
0.0366	0.99874	0.6230	232.07	0.64
0.0532	1.00082	0.6290	232.14	0.64
0.0699	1.00291	0.6373	232.19	0.64
0.0869	1.00500	0.6445	232.27	0.64
0.1041	1.00710	0.6518	232.34	0.64
	0.08 mol kg^{-1} aqueous L-ascorbic acid solution			
		$T/K = 298.15$		
0.0202	1.00497	0.9385	229.13	0.64
0.0366	1.00707	0.9575	229.32	0.64
0.0532	1.00917	0.9766	229.57	0.64
0.0699	1.01128	0.9992	229.70	0.64
0.0869	1.01339	1.0172	229.76	0.64
0.1041	1.01551	1.0376	229.89	0.64

Contd...

		T/K = 308.15		
0.0202	1.00178	0.7517	231.58	0.64
0.0366	1.00385	0.7648	231.7	0.64
0.0532	1.00592	0.7802	231.85	0.64
0.0699	1.00801	0.7934	231.99	0.64
0.0869	1.01010	0.8054	232.03	0.64
0.1041	1.01219	0.8210	232.16	0.64
		T/K = 318.15		
0.0202	0.99795	0.6189	232.97	0.65
0.0366	1.00000	0.6249	233.15	0.65
0.0532	1.00206	0.6309	233.21	0.65
0.0699	1.00414	0.6428	233.26	0.65
0.0869	1.00621	0.6476	233.37	0.65
0.1041	1.00830	0.6549	233.45	0.65

[a]m is the molality of lactose in aqueous lactose solutions in mol.kg^{-1}.

The apparent molar volumes ϕ_V of lactose monohydrate in various aqueous L-ascorbic acid solutions were obtained from the following relation:

$$\phi_V = \frac{M}{\rho} - \frac{1000(\rho - \rho_1)}{m\rho\rho_1} \tag{1}$$

where M is the molar mass of lactose monohydrate, m is its molality in the solution, ρ_1 and ρ are the densities of the solvent and solution, respectively. Uncertainties in ϕ_V values were within $\pm(0.11 - 0.62) \times 10^{-6} \, \text{m}^3 \cdot \text{mol}^{-1}$. Table 9.2 shows that apparent molar volumes ϕ_V increase with increasing temperature and L-ascorbic acid content in the aqueous solutions under study. Such trends in apparent molar volumes suggest that the interactions between solute and solvent as well as those between solute-solute or solute-cosolute change with solvent compositions and temperature. However, more clear information regarding solute-solute and solute-solvent interactions can be had

Chapter IX

from limiting apparent molar volumes at infinite dilution or rather in infinitesimal concentration, *i.e.*, standard partial molar volumes ϕ_V^0 of the solute. Due to the linear relationship between ϕ_V and square root of molar concentrations ($\sqrt{m}$) in the studied concentration range of lactose monohydrate at all experimental temperatures, Masson equation was used to determine the standard partial molar volumes ϕ_V^0 [17]:

$$\phi_V = \phi_V^0 + S_V^* \sqrt{m} \tag{2}$$

where intercept is equal to the standard partial molar volume ϕ_V^0 of the solute and slope is equal to the pair-wise interaction coefficient S_V^*. Actually the ϕ_V^0 values were determined by fitting the dilute data ($m < 0.1$) to Eq. (2) using a weighted least squares linear regression and the correlation coefficient (R^2) values were within the range 0.99337-0.99941. The weighing factors were set equal to inverse of the variance of the ϕ_V values for each data point. The intercept ϕ_V^0, *i.e.,* the standard partial molar volume provides a measure of solute-solvent interactions and the slope S_V^* provides information regarding solute-solute interactions. The values of ϕ_V^0 and S_V^* along with standard deviations (σ) for lactose monohydrate in different aqueous L-ascorbic acid solutions at the experimental temperatures are reported in Table 9.3. Table 9.3 shows that ϕ_V^0 values are positive and increase when both the temperature and L-ascorbic acid content in the solvents increase. Such trends in ϕ_V^0 values suggest the presence of strong solute-solvent interactions, which further increases with higher concentrations of L-ascorbic acid in the ternary solutions at elevated temperatures and these trends in ϕ_V^0 values are similar to those in ϕ_V values (as listed in Table 9.2) for the studied solutions. These facts may be ascribed to increase in the solvation of the solutes at higher cosolute concentrations. However, at higher temperatures probably solvent molecules from the loose solvation shell or secondary solvation shell of the solute get released into the bulk solvent leading to increase of ϕ_V^0 values [18]. Dependence of ϕ_V^0 values on the solvent composition is depicted in Fig. 9.2.

Table 9.3. Standard partial molar volumes (ϕ_V^0), the slopes (S_V^*) and corresponding standard deviations (σ) for lactose monohydrate in aqueous L-ascorbic acid solutions at T = (298.15 to 318.15) K.

T/K	$\dfrac{\phi_V^0 \times 10^6}{\mathrm{m^3 \cdot mol^{-1}}}$	$\dfrac{S_V^* \times 10^6}{\mathrm{m^3 \cdot kg^{1/2} \cdot mol^{-3/2}}}$	$\dfrac{\sigma \times 10^6}{\mathrm{m^3 \cdot mol^{-1}}}$
		0.00 [a]	
298.15	226.99 (±1.22)	2.92 (±0.09)	0.14
308.15	228.19 (±0.95)	2.73 (±0.11)	0.16
318.15	229.60 (±1.17)	2.38 (±0.07)	0.11
		0.02 [a]	
298.15	227.19 (±0.96)	4.21 (±0.24)	0.10
308.15	228.51 (±0.79)	4.11 (±0.26)	0.12
318.15	229.94 (±0.85)	2.94 (±0.17)	0.16
		0.04 [a]	
298.15	227.35 (±0.92)	4.65 (±0.29)	0.12
308.15	229.20 (±0.97)	3.79 (±0.62)	0.11
318.15	230.52 (±1.10)	2.85 (±0.14)	0.11
		0.06 [a]	
298.15	228.21 (±1.11)	3.93 (±0.13)	0.06
308.15	230.25 (±1.12)	3.11 (±0.12)	0.08
318.15	231.68 (±0.94)	2.02 (±0.13)	0.16
		0.08 [a]	
298.15	228.54 (±1.07)	4.26 (±0.08)	0.04
308.15	231.10 (±1.11)	3.24 (±0.06)	0.07
318.15	232.63 (±1.12)	2.49 (±0.08)	0.06

[a] Molality of L-ascorbic acid in aqueous solutions in mol.kg^{-1}.
Standard errors are given in parenthesis.

The volumetric coefficient S_V^* characterizes pair-wise interactions between the solvated species or solute-solute interactions in solution phase [19]. Its sign is

determined by the interactions between the solute species. In this study, S_V^* values were found to positive for all the studied solutions and follow a reversed trend in comparison to that followed by ϕ_V^0 values at the studied concentration range of the solute and the cosolute in solution phase. For a weak ionic species like L-ascorbic acid and a non ionic species like lactose monohydrate, positive S_V^* values suggest that the pair-wise interaction between the solute-solute or the solute-cosolute is dominated by the charged functional groups and such interactions probably diminishes with temperature rise due to solvent induced cosphere overlap or solute-solute hydrophobic interactions [20]. Anyway, the S_V^* values are always smaller as compared to the ϕ_V^0 values for all the studied solutions and this fact indicates that the solute-solvent interactions play a dominant role over the solute-solute interactions in characterizing the volumetric properties of studied systems.
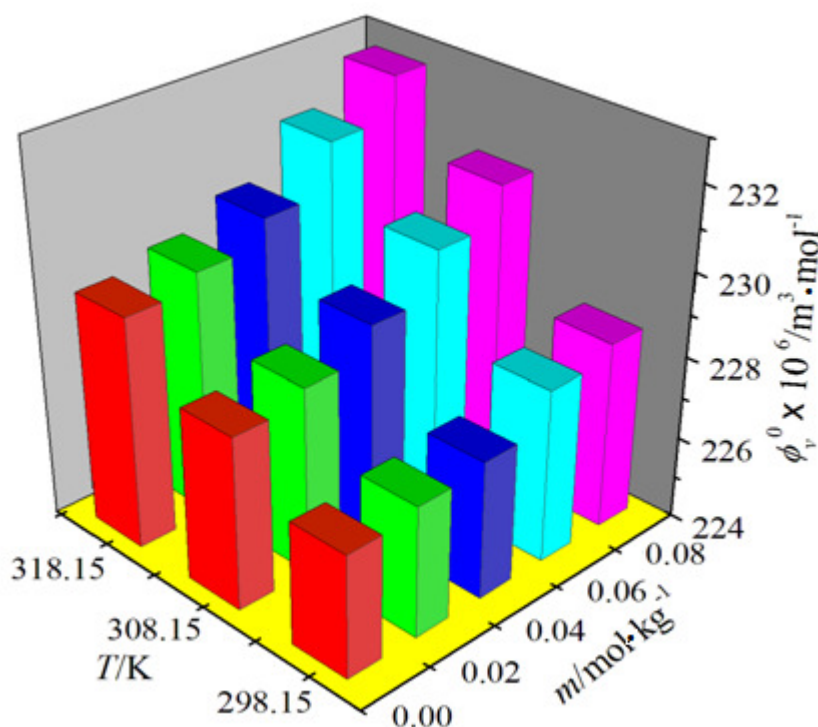
Fig. 9.2. Dependence of standard partial molar volumes (ϕ_V^0) for lactose monohydrate on the molality (*m*) of L-ascorbic acid in aqueous solutions at $T = (298.15\text{-}318.15)$ K.

Chapter IX

9.3.2. Standard transfer volumes

Limiting thermodynamic transfer properties provide information about the solute-cosolute interaction, because at infinitesimal concentration the interactions between individual solute molecules are negligible. Hence $\Delta_t \phi_V^0$ is free from solute-solute interactions and provides valuable information about solute-cosolute interactions. The standard partial molar volume of transfer ($\Delta_t \phi_V^0$) were obtained from the relation:

$$\Delta_t \phi_V^0 = \phi_V^0 [\text{Lactose monohydrat e} + \text{water} + \text{ascorbic acid}]$$
$$- \phi_V^0 [\text{ Lactose monohydrat e} + \text{water }] \qquad (3)$$

The $\Delta_t \phi_V^0$ values are depicted in Fig. 9.3 as a function of molality of L-ascorbic acid in the aqueous solutions. $\Delta_t \phi_V^0$ values are positive at all the experimental temperatures and increases monotonically with the increase in L-ascorbic acid content in ternary solutions. According to the cosphere overlap model, as developed by Friedman and Krishnan [21] "the overlap of hydration cospheres of two ionic or polar species results in an increase in volume but that of hydration cospheres of hydrophobic-hydrophobic and ion-hydrophobic group results in volume decrease". The positive $\Delta_t \phi_V^0$ values thus indicate that solute-hydrophilic and hydrophilic-hydrophilic group interactions dominate over solute-hydrophobic, hydrophobic-hydrophobic and hydrophilic-hydrophobic interactions and the overall effect of the overlap of the hydration cospheres of lactose monohydrate and L-ascorbic acid reduces the electrostriction of water in the studied solutions. Such decreased electrostriction results in a concomitant increase in volume and this effect also increases with increasing molality of L-ascorbic acid in the ternary solutions.

The partial molar volume of a solute may also be explained with the aid of a simple model [22-23] as given by the relation:

$$\phi_V^0 = \phi_{VW} + \phi_{Void} - \phi_S \qquad (4)$$

where ϕ_{VW}, the van der Waals volume; ϕ_{Void}, the volume associated with voids or empty space and ϕ_S stands for the shrinkage volume due to electrostriction.
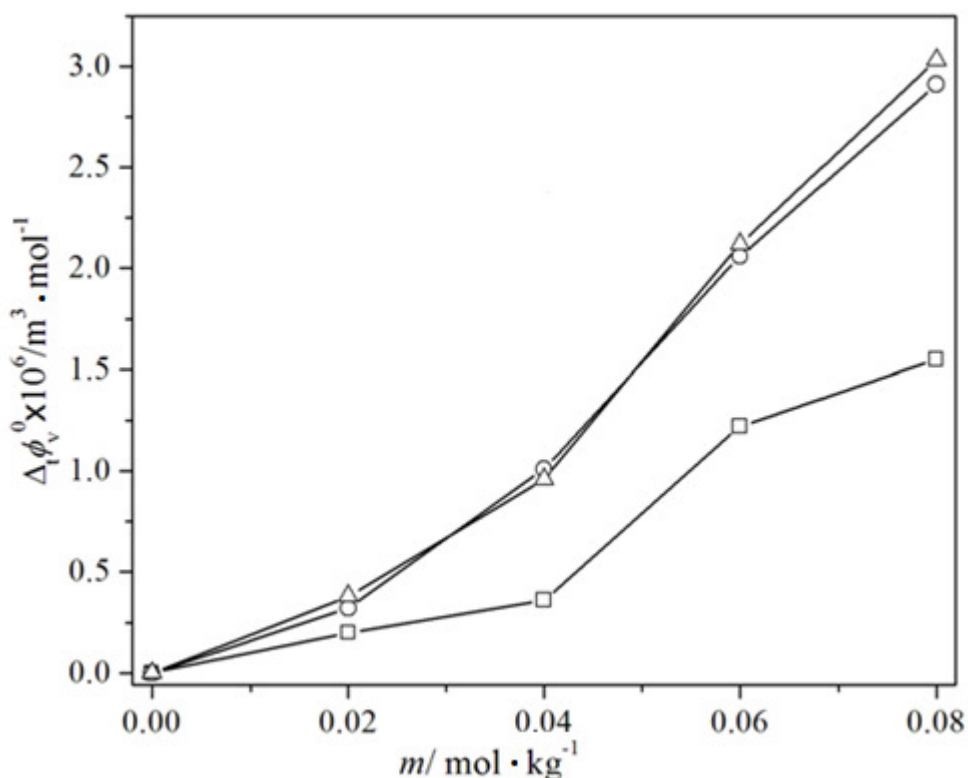
Fig. 9.3. Plots of standard partial molar volume of transfer ($\Delta_t \phi_V^0$) for lactose monohydrate on the molality of L-ascorbic acid in aqueous solutions at $T = (298.15\text{-}318.15)$ K. Symbols: $\square$, $T = 298.15$ K; $\circ$, $T = 308.15$ K; $\triangle$, $T = 318.15$ K.

With the assumption that ϕ_{VW} and ϕ_{Void} to have same magnitudes in water and in aqueous L-ascorbic acid solutions for the same solute (*i.e.*, lactose monohydrate), the increase in ϕ_V^0 values and the concomitant positive $\Delta_t \phi_V^0$ values can be attributed to the decrease in the shrinkage volume (ϕ_S) of water by lactose monohydrate in presence of L-ascorbic acid. This fact suggests that L-ascorbic acid has a dehydration effect on the hydrated lactose monohydrate. Anyway, the interactions between lactose monohydrate and L-ascorbic acid can roughly be summarized as: (i) the hydrophilic-ionic group interactions between OH groups of lactose and the ions of L-ascorbic acid, (ii) hydrophilic-hydrophilic interactions between OH groups of lactose and ascorbate anion of L-ascorbic acid through hydrogen bonding, (iii) hydrophilic-hydrophobic interactions between OH groups of lactose and non-polar groups of L-ascorbic acid and (iv) hydrophobic-hydrophobic interactions between non-polar

groups of lactose and non-polar groups of L-ascorbic acid. According to co-sphere overlap model (i) and (ii) type interactions contribute positively, whereas (iii) and (iv) type interactions contribute negatively to the $\Delta_t \phi_V^0$ values. Therefore, for the present study solute-hydrophilic and hydrophilic-hydrophilic group interactions play predominant roles in characterizing the volumetric properties of the studied ternary solutions. However, standard partial molar volume of a solute reflects a overall result of several solute-solute, solute-solvent and solute-cosolute interactions prevailing in solutions like: electrostatic interactions between the local charge on the solute, cosolute or its ions and the dipole moment of H_2O, interlocking packing interactions of the ions, solutes or cosolutes with H_2O leading to interstitial packing or caging and also solvation and other polar-ionic group (H-bonding) interactions between different polar and non-polar groups of L-ascorbic acid and lactose monohydrate; all these interactions can characterize the overall state of the solutions studied.

9.3.3. Apparent specific volumes and taste quality

Apparent molar volumes (ϕ_V) at the experimental temperatures were used to calculate the apparent specific volumes (ϕ_{Vsp}) of lactose monohydrate in these solutions by using the following equation (Table 9.3):

$$\phi_{Vsp} = \frac{\phi_V}{M} \qquad (5)$$

Apparent specific volume gives an idea about its relationship with taste quality in the order salty < sour < sweet < bitter [24-26]. The whole human taste range lies with apparent specific volumes between 0.1 and 0.95 $cm^3 \cdot g^{-1}$, *i.e.*, salty [ϕ_{Vsp} <0.33 $cm^3 \cdot g^{-1}$], sour [ϕ_{Vsp} = 0.33-0.52 $cm^3 \cdot g^{-1}$], sweet [ϕ_{Vsp} =0.52-0.71 $cm^3 \cdot g^{-1}$] and bitter [ϕ_{Vsp} = 0.71-0.93 $cm^3 \cdot g^{-1}$)] [27]. The ϕ_{Vsp} values for all studied lactose monohydrate solutions occur within the sweet range of taste, *i.e.*, (0.52-0.71) $cm^3 \cdot g^{-1}$. The ϕ_{Vsp} values for lactose monohydrate increase with the increase of L-ascorbic acid content and temperature. The apparent specific volumes for most of the sugars fall in the range (0.61-0.62) $cm^3 \cdot g^{-1}$ which is the centre of the sweet range, so does lactose monohydrate (0.63-0.64 $cm^3 \cdot g^{-1}$) and in the experimental solutions the ϕ_{Vsp} values

changes up to 0.65 cm^3.g^{-1}; so although lactose monohydrate retains its sweet taste in the experimental solutions, its sweetness seems to decrease a little in the studied solutions.

9.3.4. Apparent molar expansibilities

The apparent molar expansibilities (ϕ_E) of lactose monohydrate solutions were calculated from the apparent molar volumes (ϕ_V) and densities (ρ) at the experimental temperatures by using the relation [28]:

$$\phi_E = \alpha\phi_V + \frac{1000(\alpha - \alpha_1)}{m\rho_1} \tag{6}$$

where α_1 and α and are the coefficients of isobaric thermal expansion of the solvent and the solution, respectively and other symbols have their usual significance. α and α_1 are defined as: $\alpha = -\rho^{-1}(\partial\rho/\partial T)_P$ and $\alpha_1 = -\rho_1^{-1}(\partial\rho_1/\partial T)_P$. The uncertainty in the coefficients of isobaric thermal expansion was $\pm 2 \cdot 10^{-5} \text{K}^{-1}$ and the uncertainty in ϕ_E values was within $\pm (0.001 - 0.002) \times 10^{-6} \text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, respectively. The standard partial molar expansibilities (ϕ_E^0) were then determined from the relation [29]:

$$\phi_E = \phi_E^0 + S_E \sqrt{m} \tag{7}$$

The ϕ_E^0 value is an important measure of solute-solvent interactions and it helps to interpret the long-range structure making or breaking properties of solutes [30]. The ϕ_E^0 values along with its corresponding errors for different experimental solutions at different temperatures are given in Table 9.4. It shows that ϕ_E^0 values are positive and increase with a rise in the experiment temperatures. Such a trend in ϕ_E^0 values corroborates to the structural perturbation influenced by the gradual appearance of 'packing effect' or 'caging effect' for lactose monohydrate in the studied solutions [31]. However, at elevated temperatures probably owing to the fast molecular motions the distinction between water structure within the hydration or solvation shell and the bulk water structure diminishes. Anyway as par Hepler' proposition [31] if the term

$\left(\partial\phi_E^0/\partial T\right)_P$ is positive, the solute is a structure maker otherwise it is a structure breaker. The $(\partial\phi_E^0/\partial T)_P$ values can be had from the slope of a linear fit of ϕ_E^0 values (a least squares linear regression used) against experimental temperature (T) with the correlation coefficients (R^2) within the range 0.94923-0.99545. The $\left(\partial\phi_E^0/\partial T\right)_P$ values for the present experiment are given in Table 9.4. It shows that the $\left(\partial\phi_E^0/\partial T\right)_P$ values are positive in all the aqueous L-ascorbic acid solutions. Thus lactose monohydrate appears to act a net structure maker in aqueous L-ascorbic acid solutions and the studied systems are characterized by the predominance of hydrophobic hydration over the electrostriction of water by the solute and cosolute molecules as far as present investigation is concerned.

Table 9.4 Standard partial molar expansibilities (ϕ_E^0) for lactose monohydrate in aqueous solutions of L-ascorbic acid at $T =$ (298.15 to 318.15) K.

Solvent	$\phi_E^0 \cdot 10^{-5}$ $m^3 \cdot mol^{-1} \cdot K^{-1}$			$S_E \cdot 10^{-5}$ $m^3 \cdot kg^{1/2} \cdot mol^{-1} \cdot K^{-1}$			$\left(\dfrac{\partial\phi_E^0}{\partial T}\right)_P \cdot 10^{-8}$ $m^3 \cdot mol^{-1} \cdot K^{-2}$
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K	
0.00 [a]	5.04 (±0.08)	5.12 (±0.08)	5.15 (±0.08)	-3.21 (±0.04)	-3.31 (±0.04)	-3.27 (±0.04)	5.22
0.02 [a]	2.28 (±0.09)	2.29 (±0.09)	2.33 (±0.08)	-3.68 (±0.05)	-3.71 (±0.05)	-3.69 (±0.01)	2.37
0.04 [a]	3.72 (±0.01)	3.76 (±0.01)	3.79 (±0.01)	-1.26 (±0.08)	-1.28 (±0.08)	-1.29 (±0.08)	3.91
0.06 [a]	9.26 (±0.01)	9.36 (±0.01)	9.45 (±0.01)	-1.10 (±0.07)	-1.02 (±0.08)	-1.03 (±0.07)	9.75
0.08 [a]	6.06 (±0.01)	6.13 (±0.01)	6.19 (±0.01)	-3.45 (±0.06)	-3.54 (±0.06)	-3.53 (±0.06)	6.39

[a] Molality of L-ascorbic acid in aqueous solutions in mol.kg^{-1}. Standard errors are given the parenthesis.

9.3.5. UV-visible spectroscopy

The absorption spectra of lactose monohydrate in different aqueous L-ascorbic acid solutions at 298.15 K are shown in Fig. 9.4. No distinct absorption bands for the aqueous solution of lactose monohydrate $(1\cdot10^{-4}\,mol\cdot L^{-1})$ in the wavelength range 200-300 nm was observed. However, gradual addition of the aqueous L-ascorbic acid solution $(1\cdot10^{-4}\,mol\,L^{-1}$, 40 μL at each step) to this solution a peak at 250 nm due to $\pi \rightarrow \pi^{*}$ transition of L-ascorbic acid only develops and its intensity increases as the concentration of L-ascorbic acid increases further at each step of addition. The absorption spectra of lactose monohydrate $(1\cdot10^{-4}\,mol\cdot L^{-1})$ in different aqueous solutions of L-ascorbic acid at 298.15 K are shown in Fig. 9.5.

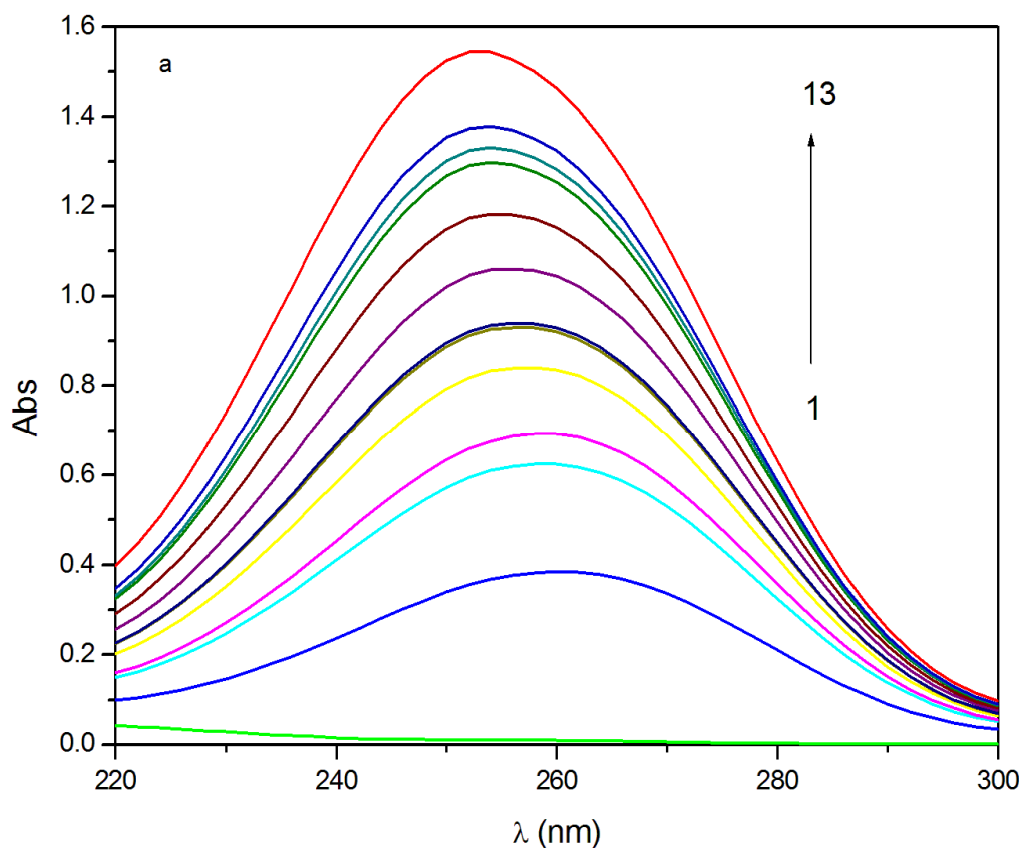**Fig. 9.4.** Changes in the UV-Visible absorption spectra of lactose monohydrate ($1\cdot10^{-4}\,mol\cdot L^{-1}$) in different aqueous L-ascorbic acid solutions at 298.15K with the following molarities of L-ascorbic acid $(1\cdot10^{-4}\,mol\cdot L^{-1})$: 1, 0.000; 2, 0.0099; 3, 0.0196; 4, 0.0291; 5, 0.0385; 6, 0.0476; 7,0.0566; 8, 0.0654; 9, 0.0740; 10, 0.0826; 11, 0.0909; 12, 0.0991; 13, 0.1071.
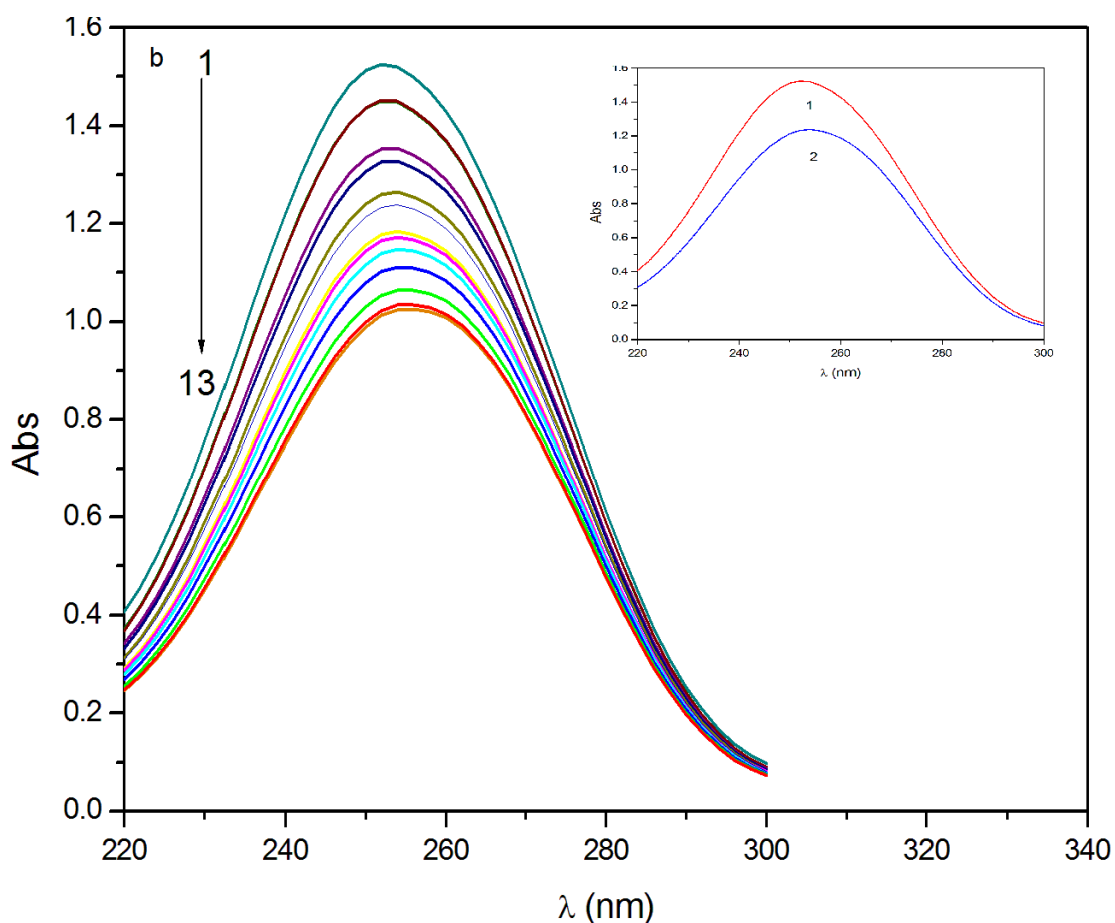
Fig. 9.5. Changes in the UV-Visible absorption spectra of lactose monohydrate in aqueous L-ascorbic acid($1 \cdot 10^{-4}\,\text{mol} \cdot \text{L}^{-1}$) at 298.15 K with the following molarities of lactose monohydrate ($1 \cdot 10^{-4}\,\text{mol} \cdot \text{L}^{-1}$): 1, 0.000; 2, 0.0099; 3, 0.0196; 4, 0.0291; 5, 0.0385; 6, 0.0476; 7,0.0566; 8, 0.0654; 9, 0.0740; 10, 0.0826; 11, 0.0909; 12, 0.0991; 13, 0.1071 Inset: 1, L-ascorbic acid in water (5.10^{-5} mol.L^{-1}); 2, average of absorption spectra (1to 13) at 298.15K.

The absorption spectrum of the aqueous L-ascorbic acid ($1 \cdot 10^{-4}\,\text{mol} \cdot \text{L}^{-1}$) solution has an absorption band in the wavelength range 220-300 nm and gives a peak at 250 nm. However, on gradual addition of the aqueous solution of lactose monohydrate ($1 \cdot 10^{-4}\,\text{mol}\,\text{L}^{-1}$, 40 µL at each step) to this solution the absorption peak at 250 nm red shifted to 254 nm, *i.e.,* bathochromic shift. This band at 250 nm is due to $\pi \rightarrow \pi^{*}$ transition involving orbitals of the C=C bond [32] present in L-ascorbic acid (H$_2$A); which remains mainly in the enol form [33] due to conjugation of the

C=C bond with C=O group; also L-ascorbic acid (H$_2$A) remains presumably in equilibrium with its mono anion (HA$^-$) and a proton (H$^+$) in the pH range 2.86-3.12 for the aqueous L-ascorbic acid solutions [34] used. Therefore, this bathochromic shift in absorbance of L-ascorbic acid can tentatively be ascribed to various possible interactions between lactose monohydrate and L-ascorbic acid as described above.

9.3.6. Viscometric results.

As lactose monohydrate behaves as a non-electrolyte, solution viscosities were analyzed with the modified Jones-Dole equation [35, 36]

$$\eta_r = 1 + Bc \qquad (7)$$

where $\eta_r = \eta/\eta_1$; η_1, η and c are the viscosities of solvent, the viscosities of solution and molarity of the solute in the solutions, respectively. The viscosity B-coefficients were calculated by least squares linear regression analysis. Viscosity B-coefficients depend on solute-solvent interactions. Table 9.5 shows that the viscosity B-coefficients are positive and increase with a rise in L-ascorbic acid content in the ternary solutions. These results thus suggest strong solute-solvent interactions in the ternary solutions and net structural enhancement at higher L-ascorbic acid concentrations. Such interactions are also well indicated by the increase in solution viscosities induced by augmentation of the L-ascorbic acid content in the ternary solutions. However, the viscosity B-coefficients decrease as the experimental temperature increases and supports our earlier proposition that solvent molecules from the loose solvation shell or secondary solvation shell of the solute get released into the bulk solvent. The sign of $(\partial B/\partial T)$ values also provide important information regarding the structure making or structure breaking ability of the solute in the solvent media [37, 38]. The $(\partial B/\partial T)$ values are negative for a structure maker and thus the temperature dependence of the viscosity B-coefficients also supports structure-making ability of lactose in aqueous L-ascorbic acid solutions.

We have also calculated solvation or hydration numbers (S_n) for lactose monohydrate using the relation [39]: $S_n = B/\phi_V^0$. S_n is indicative of the formation of a primary solvation sphere around a solute. The range $S_n \approx 0 - 2.5$ indicates unsolvated solutes [39] and higher S_n values indicate solvated solutes with primary solvation sphere.

Table 9.5. Viscosity *B*-coefficients of lactose monohydrate with the correlation coefficients R^2, standard deviations σ for linear regression of Eq. (7) along with the solvation number S_n in aqueous solutions of L-ascorbic acid at $T = (298.15$ to $318.15)$ K.

Parameters	298.15 K	308.15 K	318.15 K
		$0.00^{\,a}$	
$\dfrac{B\times10^3}{\mathrm{m^3\cdot mol^{-1}}}$	1.311 (±0.004)	1.092 (±0.009)	0.681 (±0.003)
S_n	5.77 (±0.02)	4.79 (±0.03)	2.96 (±0.01)
R^2	0.99974	0.99997	0.99982
σ	0.002	0.001	0.005
		$0.02^{\,a}$	
$\dfrac{B\times10^3}{\mathrm{m^3\cdot mol^{-1}}}$	1.329 (±0.006)	1.119 (±0.008)	0.709 (±0.006)
S_n	5.85 (±0.02)	4.90 (±0.03)	3.08 (±0.01)
R^2	0.99974	0.99997	0.99982
σ	0.004	0.001	0.005
		$0.04^{\,a}$	
$\dfrac{B\times10^3}{\mathrm{m^3\cdot mol^{-1}}}$	1.335 (±0.003)	1.130 (±0.008)	0.723 (±0.005)
S_n	5.87 (±0.03)	4.93 (±0.02)	3.13 (±0.02)
R^2	0.99999	0.99993	0.99993
σ	0.004	0.001	0.006
		$0.06^{\,a}$	
$\dfrac{B\times10^3}{\mathrm{m^3\cdot mol^{-1}}}$	1.342 (±0.005)	1.148 (±0.005)	0.747 (±0.006)
S_n	5.88 (±0.03)	4.98 (±0.01)	3.22 (±0.02)

Contd...

R^2	0.99998	0.99999	0.99996
σ	0.005	0.002	0.007
		0.08 [a]	
$\dfrac{B \times 10^3}{\mathrm{m}^3 \cdot \mathrm{mol}^{-1}}$	1.356 (±0.004)	1.164 (±0.005)	0.762 (±0.005)
S_n	5.93 (±0.01)	5.04 (±0.01)	3.27 (±0.0.1)
R^2	0.99999	0.99999	0.99999
σ	0.005	0.002	0.007

[a] Molality of L-ascorbic acid in aqueous solutions in mol.kg^{-1}.
Standard errors are given the parenthesis.

So an inspection of S_n values given in Table 9.5 indicated that lactose monohydrate remain solvated with primary solvation spheres in the aqueous solutions investigated as already discussed on the basis of ϕ_V^0 values.

Similar to $\Delta_t\phi_V^0$ values, viscosity B-coefficients of transfer ($\Delta_t B$) for lactose monohydrate from water to aqueous L-ascorbic acid solutions were determined by using the relation:

$$\Delta_t B = B[\text{Lactose monohydrat e} + \text{water} + \text{ascorbic acid}]$$
$$- B[\text{Lactosemon ohydrate} + \text{water}] \qquad (9)$$

The $\Delta_t B$ values are depicted in Fig. 9.6 as a function of L-ascorbic acid molality in aqueous solutions and simply concur with the trends of solute-cosolute interactions reflected by $\Delta_t\phi_V^0$ values.
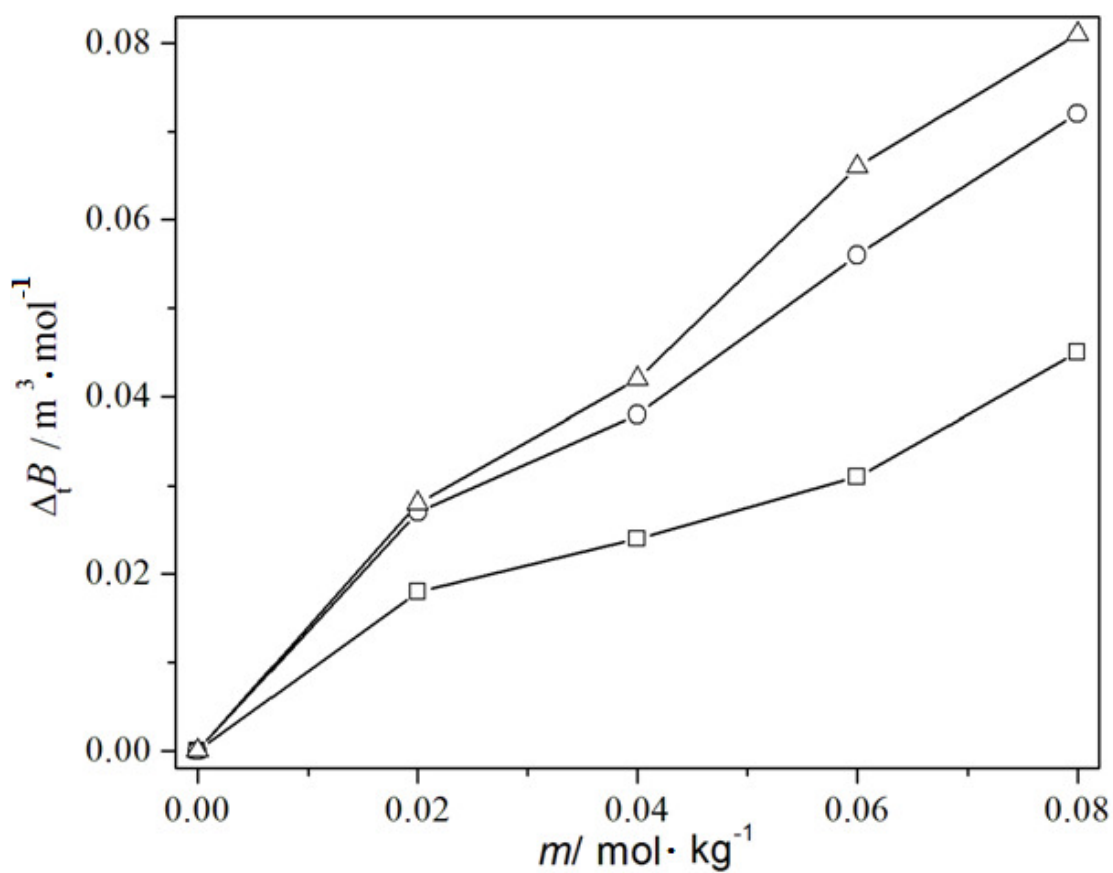
Fig. 9.6. Plots of viscosity B-coefficients of transfer ($\Delta_t B$) for lactose monohydrate on the molality of L-ascorbic acid in aqueous solutions at $T = (298.15\text{-}318.15)$ K. Symbols: $\square$, $T = 298.15$ K; $\circ$, $T = 308.15$ K; $\triangle$, $T = 318.15$ K.

9.3.7. Thermodynamics of viscous flow

Based on Feakins' transition state theory of relative viscosity [37], Gibbs free energy of activation per mole of solute ($\Delta\mu_2^{0\neq}$) and Gibbs free energy of activation per mole of solvent ($\Delta\mu_1^{0\neq}$) can be obtained from the viscosity B- coefficients using the relations [40]:

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT\ln(\eta_1 \phi_{V,1}^0 / hN_A) \qquad (10)$$

$$\Delta\mu_2^{0\neq} = \Delta\mu_1^{0\neq} + RT(1000B + \phi_{V,2}^0 - \phi_{V,1}^0)/\phi_{V,1}^0 \qquad (11)$$

where N_A, $\phi_{V,1}^0$ are the Avogadro's number and the partial molar volume of the solvent, respectively. The other symbols have their usual significances.

Table 9.6. Values of $\phi_{V.2}^0 - \phi_{V.1}^0$, $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$, $\Delta H_2^{0\neq}$ and $T\Delta S_2^{0\neq}$ for lactose monohydrate in aqueous solutions of L-ascorbic acid at T = (298.15 to 318.15) K.

Parameters	298.15 K	308.15 K	318.15 K
		0.00 [a]	
$\dfrac{(\phi_{V,2}^0 - \phi_{V,1}^0)\times 10^6}{\mathrm{m^3 \cdot mol^{-1}}}$	208.88	209.96	211.23
$\dfrac{\Delta\mu_1^{0\neq}}{\mathrm{kJ \cdot mol^{-1}}}$	9.17	8.94	8.76
$\dfrac{\Delta\mu_2^{0\neq}}{\mathrm{kJ \cdot mol^{-1}}}$	216.99	191.98	137.18
$\dfrac{T\Delta S_2^{0\neq}}{\mathrm{kJ \cdot mol^{-1}}}$	1189.66	1229.56	1269.46
$\dfrac{\Delta H_2^{0\neq}}{\mathrm{kJ\cdot mol^{-1}}}$	1406.64	1421.54	1406.64
		0.02 [a]	
$\dfrac{(\phi_{V,2}^0 - \phi_{V,1}^0)\times 10^6}{\mathrm{m^3 \cdot mol^{-1}}}$	209.06	210.22	211.59
$\dfrac{\Delta\mu_1^{0\neq}}{\mathrm{kJ \cdot mol^{-1}}}$	9.19	8.97	8.78
$\dfrac{\Delta\mu_2^{0\neq}}{\mathrm{kJ \cdot mol^{-1}}}$	219.46	195.26	141.40
$\dfrac{T\Delta S_2^{0\neq}}{\mathrm{kJ \cdot mol^{-1}}}$	1163.28	1202.70	1241.83
$\dfrac{\Delta H_2^{0\neq}}{\mathrm{kJ\cdot mol^{-1}}}$	1366.74	1381.60	1366.74

Contd...

	0.04 [a]		
$\dfrac{(\phi_{V,2}^0 - \phi_{V,1}^0) \times 10^6}{\text{m}^3 \cdot \text{mol}^{-1}}$	209.25	210.94	212.09
$\dfrac{\Delta\mu_1^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	9.21	8.99	8.81
$\dfrac{\Delta\mu_2^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	220.58	197.15	143.28
$\dfrac{T\Delta S_2^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	1152.31	1190.95	1229.60
$\dfrac{\Delta H_2^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	1372.89	1388.11	1372.89
	0.06 [a]		
$\dfrac{(\phi_{V,2}^0 - \phi_{V,1}^0) \times 10^6}{\text{m}^3 \cdot \text{mol}^{-1}}$	210.03	212.01	213.27
$\dfrac{\Delta\mu_1^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	9.24	9.00	8.83
$\dfrac{\Delta\mu_2^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	220.86	199.99	146.73
$\dfrac{T\Delta S_2^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	1104.99	1142.05	1179.12
$\dfrac{\Delta H_2^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	1325.84	1342.04	1325.84
	0.08 [a]		
$\dfrac{(\phi_{V,2}^0 - \phi_{V,1}^0) \times 10^6}{\text{m}^3 \cdot \text{mol}^{-1}}$	210.38	212.79	214.25

$\dfrac{\Delta\mu_1^{0\neq}}{kJ\cdot mol^{-1}}$	9.26	9.03	8.84
$\dfrac{\Delta\mu_2^{0\neq}}{kJ\cdot mol^{-1}}$	223.03	201.68	149.25
$\dfrac{T\Delta S_2^{0\neq}}{kJ\cdot mol^{-1}}$	1099.80	1136.69	1173.58
$\dfrac{\Delta H_2^{0\neq}}{kJ\cdot mol^{-1}}$	1322.83	1338.37	1322.83

[a] Molality of L-ascorbic acid in water in mol. kg⁻¹.

For the aqueous L-ascorbic acid solutions (used as solvents), $\phi_{V,1}^0$ is taken as the mole fraction average of molecular weights of L-ascorbic acid and water normalized by densities at the experimental temperatures. Over a short range of temperature the standard partial molar enthalpy ($\Delta H_2^{0\neq}$) and entropy ($\Delta S_2^{0\neq}$) of activation for viscous flow of a solution can approximately be had from the relation:

$$\Delta S_2^{0\#} = -d(\Delta\mu_2^{0\#})/dT \qquad (12)$$

$$\Delta H_2^{0\neq} = \Delta\mu_2^{0\neq} + T\Delta S_2^{0\neq} \qquad (13)$$

The parameters $(\phi_{V,2}^0 - \phi_{V,1}^0)$, $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$, $\Delta H_2^{0\neq}$ and $T\Delta S_2^{0\neq}$ are given in Supplementary Table 9.6. $\Delta\mu_1^{0\neq}$ values are positive and are almost invariant of the solvent compositions at a particular temperature but decrease slightly with a rise in experimental temperature. $\Delta\mu_2^{0\neq}$ values are positive and much greater than the $\Delta\mu_1^{0\neq}$ values for all the studied solutions at all the experimental temperatures. These facts suggest that the solute-solvent interactions in the ground state are stronger than in the transition state. Hence in the transition state solvation of lactose monohydate is less favored in free energy terms. According to Feakins *et al.* [37], the greater the value of $\Delta\mu_2^{0\neq}$, the greater is the structure-promoting tendency of a solute and the positive $\Delta\mu_2^{0\neq}$ values for lactose monohydrate in the studied aqueous solutions suggest it to be a net structure promoter. However, positive $\Delta H_2^{0\neq}$ values suggest the viscous flow to be endothermic and promoted by positive $\Delta S_2^{0\neq}$ values (given in Table 9.6), *i.e.*,

attainment of the transition state for viscous flow involves breaking or distortion of intermolecular bonds. Thus the viscous flow of the studied aqueous solutions seems to be entropy driven processes.

9.4. Conclusion

Different volumetric and viscometric parameters derived for the studied ternary solutions suggests that solute-solvent interactions are predominant for lactose monohydrate in aqueous L-ascorbic acid solutions and such interactions get strengthened further with the increase of both temperature and L-ascorbic acid concentrations. The positive $\left(\partial\phi_E^0/\partial T\right)_P$ values suggest that the structure making behavior of lactose monohydrate in the aqueous L-ascorbic acid solutions. S_n values indicated that the lactose monohydrate remain solvated with primary solvation spheres in the aqueous L-ascorbic acid solutions. The apparent specific volumes increase with the increasing concentration of L-ascorbic acid and therefore the sweetness decreases. Positive $\Delta\mu_2^{0\neq}$ values indicate that solute-solvent interactions in the ground state are stronger than in the transition state and the viscous flow is entropy driven endothermic process as confirmed by the positive $\Delta H_2^{0\neq}$ and $\Delta S_2^{0\neq}$ values.

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