

CHAPTER IV

Solution thermophysics of L-ascorbic acid in aqueous tetrabutylammonium hydrogen sulphate*

4.1. Introduction

The volumetric and viscometric behaviour of multicomponent solution plays an important role in industrial sectors concerning mass transfer, heat transfer and fluid flow [1]. They are used as tools to develop models for the engineering applications, specifically in biochemical engineering involving the thermodynamic and transport properties of solutions. So studies on the properties of multicomponent solution systems have evoked a lot of interests [2, 3]. It is well known that ascorbic acid (vitamin C) is a naturally occurring water-soluble vitamin with antioxidant properties. It is not only required for the metabolism of folic acid, tyrosine, phenylalanine, histamine, *etc.*, but also essential for the synthesis of collagen that contributes to the structure of muscles and bones [4]. It is used as an anti-ageing agent as it protects the body tissues and cells against oxidative damage from free radicals and reactive oxygen derivatives. It improves the elasticity of skin and thus reduces wrinkles due to its involvement in proline and lysine hydroxylation in collagen biosynthesis. Deficiency of ascorbic acid in human can cause several diseases like scurvy, anaemia, gum problems, muscle degradation and neurotic disorders, *etc.* Hence it is used as a food additive (code E300).

Salts solutions have profound effects on the structure and properties of vitamins. Tetraalkylammonium salts are bulky in nature and can orient water molecules around themselves depending on their alkyl chain lengths [5, 6]. Therefore, aqueous solution of tetraalkylammonium cations can stand as model systems for the study of hydrophobic hydration and salts like tetrabutylammonium hydrogen sulphate (TBAHS), an ion-pairing reagent [7], can provide information about the effect of different non-covalent interactions on the stabilities of vitamins.

Although few studies are available on various properties of L-ascorbic acid in aqueous solutions [4, 8-10], such a study on solution properties of L-ascorbic acid in aqueous TBAHS solution is not available in the literature. Hence in the present chapter we have studied the various interactions interplaying in the aqueous solutions of L-ascorbic acid in presence of TBAHS in terms of apparent molar volumes,

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standard partial molar volumes and viscosity B -coefficients, *etc.*, at $T = (298.15, 308.15 \text{ and } 318.15) \text{ K}$ under atmospheric pressure.

4.2. Experimental Section

4.2.1. Chemicals used

Reagent grade L-ascorbic acid (CAS: 50-81-7; Sigma-Aldrich, mass fraction purity > 0.990) and A. R grade TBAHS (CAS: 32503-27-8, S. D. Fine Chemicals, India; mass fraction purity > 0.985) were used for present study. Provanance and purity of the chemicals are given in chapter III. L-ascorbic acid was used as received from the vendor without further purification but it was dried in *vacuo* over anhydrous CaCl_2 for several hours before use and its melting point was found to be 463 K. TBAHS was purified by dissolving it in a 1:1 (v/v) methanol and ethanol mixture and recrystallized from diethyl ether. After filtration the salt was dried in *vacuo* for few hours and its melting point was found to be 444 K. Doubly distilled de-ionized water with a specific conductance $< 1 \cdot 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ at 298.15 K was used to prepare different aqueous solutions of TBAHS. Various aqueous solution of TBAHS (used as solvent) were prepared by mass and necessary adjustments were done to achieve exact molal concentrations ($m_{\text{TBAHS}} = 0.005, 0.010, 0.015 \text{ and } 0.020 \text{ mol}\cdot\text{kg}^{-1}$) of TBAHS in the aqueous solutions at 298.15 K. The relative error in solvent composition was about 1 %. The physical properties of these aqueous TBAHS solutions are given in Table 4.1. Stock solutions of L-ascorbic acid in different aqueous TBAHS solutions were prepared by mass and all the working solutions were prepared afresh before use by mass dilution. The mass measurements were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland) with an uncertainty of $\pm 1 \cdot 10^{-4} \text{ g}$. The conversion of molalities into molarities was accomplished by using experimental density data whenever needed [11]. Estimated uncertainty in molality of L-ascorbic acid solutions was evaluated to $\pm 1 \cdot 10^{-4} \text{ mol}\cdot\text{kg}^{-1}$. The molecular structures of l-L-ascorbic acid and tetrabutylammonium hydrogen sulfate (TBAHS) are shown in Fig. 4.1.

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Table 4.1. Densities (ρ) and viscosities (η) of different aqueous solutions of TBAHS at $T =$ (298.15 to 318.15) K.

m_{TBAHS}^a	T/K	$\frac{\rho \times 10^{-3}}{(\text{kg} \cdot \text{m}^{-3})}$	$\frac{\eta}{(\text{mPa} \cdot \text{s})}$
0.005	298.15	0.99726	0.8940
	308.15	0.99427	0.7231
	318.15	0.99044	0.6015
0.010	298.15	0.99742	0.8964
	308.15	0.99443	0.7255
	318.15	0.99060	0.6027
0.015	298.15	0.99760	0.8988
	308.15	0.99458	0.7279
	318.15	0.99079	0.6052
0.020	298.15	0.99772	0.9012
	308.15	0.99470	0.7303
	318.15	0.99095	0.6076

^a Molality of TBAHS in aqueous solutions.

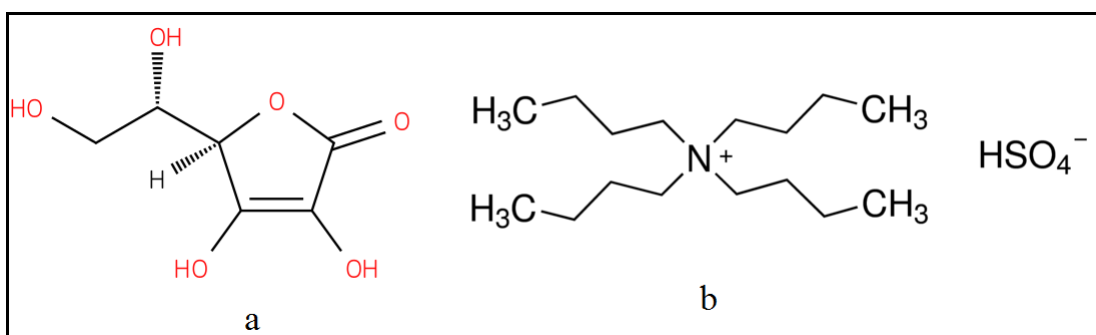


Fig. 4.1. Molecular structure of: a) L-Ascorbic acid and b) Tetrabutylammonium hydrogen sulfate.

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4.2.2 Apparatus and procedure

Densities were measured with a vibrating-tube densitometer (Anton Paar, DMA 4500M). The densitometer was calibrated at the experimental temperatures with doubly distilled, degassed water and dry air at atmospheric pressure. The temperature was automatically kept constant with an accuracy of $\pm 1 \times 10^{-2}$ K by using an automatic built-in Peltier technique. The stated repeatability and accuracy of the densities were $\pm 1 \times 10^{-5} \text{ g} \cdot \text{cm}^{-3}$ and $\pm 5 \times 10^{-5} \text{ g} \cdot \text{cm}^{-3}$, respectively. However, the estimated uncertainty of the density measurements for most of the solutions was found to be within $\pm 0.01 \text{ kg} \cdot \text{m}^{-3}$. Viscosities were measured by means of a suspended Canon-type Ubbelohde viscometer thoroughly cleaned, dried and calibrated at the experimental temperatures with triply distilled, degassed water and purified methanol [12, 13]. It was filled with an experimental liquid and placed vertically in a glass sided thermostatic bath (Julabo, Germany) maintained constant to ± 0.01 K. After attainment of thermal equilibrium, the efflux times of flow of the liquid samples were recorded with a digital stopwatch with an uncertainty of ± 0.01 s. In all determinations, an average of triplicate measurements was taken into account and adequate precautions were adopted to minimize evaporation losses during the actual measurements. The uncertainty of viscosity values was $\pm 0.003 \text{ mPa} \cdot \text{s}$. Details of density and viscosity measurement methods and techniques have been described elsewhere [14-16].

4.3. Results and discussion

The experimental values of molalities (m), densities (ρ), viscosities (η), and apparent molar volumes (ϕ_V) for the experimental solutions of L-ascorbic acid in different aqueous TBAHS solutions at various temperatures are reported in Table 4.2.

4.3.1. Standard partial molar volumes

The apparent molar volumes (ϕ_V) of L-ascorbic acid in aqueous TBAHS solutions were obtained from the following relation [17]:

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

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Table 4.2. Molalities (m), densities (ρ), viscosities (η), and apparent molar volumes (ϕ_V) of L-ascorbic acid in aqueous TBAHS solutions at $T = (298.15 \text{ to } 318.15) \text{ K}$.

m (mol · kg ⁻¹)	$\rho \cdot 10^{-3}$ (kg · m ⁻³)	η (mPa · s)	$\phi_V \cdot 10^6$ (m ³ · mol ⁻¹)
0.000 ^a			
$T/\text{K} = 298.15$			
0.0202	0.99842	0.8985	108.93
0.0365	0.99949	0.9039	109.13
0.0529	1.00056	0.9095	109.39
0.0695	1.00162	0.9161	109.52
0.0863	1.00268	0.9216	109.63
0.1032	1.00373	0.9273	109.84
$T/\text{K} = 308.15$			
0.0202	0.99539	0.7239	110.06
0.0365	0.99644	0.7282	110.37
0.0529	0.99749	0.7324	110.67
0.0695	0.99852	0.7377	110.98
0.0863	0.99954	0.7431	113.32
0.1032	1.00057	0.7477	113.47
$T/\text{K} = 318.15$			
0.0202	0.99155	0.5998	111.75
0.0365	0.99257	0.6039	112.23
0.0529	0.99359	0.6081	112.60
0.0695	0.99459	0.6122	112.94
0.0863	0.99559	0.6163	113.18
0.1032	0.99660	0.6210	113.27

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0.005 ^a			
<i>T/K = 298.15</i>			
0.0202	0.99860	0.9009	109.42
0.0365	0.99966	0.9075	109.68
0.0529	1.00072	0.913	109.83
0.0695	1.00177	0.9196	110.10
0.0862	1.00282	0.9251	110.22
0.1032	1.00387	0.9308	110.33
<i>T/K = 308.15</i>			
0.0202	0.99559	0.7264	110.56
0.0365	0.99663	0.7317	110.92
0.0529	0.99767	0.7371	111.12
0.0695	0.99870	0.7425	111.41
0.0862	0.99973	0.7467	111.54
0.1032	1.00076	0.7513	111.66
<i>T/K = 318.15</i>			
0.0202	0.99173	0.6034	112.25
0.0365	0.99275	0.6064	112.51
0.0529	0.99377	0.6105	112.66
0.0695	0.99479	0.6147	112.78
0.0862	0.99580	0.6200	112.93
0.1032	0.99680	0.6246	113.15
0.010 ^a			
<i>T/K = 298.15</i>			
0.0202	0.99873	0.9033	110.92
0.0364	0.99977	0.9099	111.06
0.0529	1.00081	0.9165	111.17

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0.0695	1.00185	0.9220	111.26
0.0862	1.00288	0.9286	111.40
0.1031	1.00390	0.9343	111.61
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<i>T/K = 308.15</i>			
0.0202	0.99573	0.7288	111.56
0.0364	0.99676	0.7341	111.76
0.0529	0.99779	0.7395	111.89
0.0695	0.99882	0.7449	111.99
0.0862	0.99984	0.7502	112.13
0.1031	1.00086	0.7548	112.26
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<i>T/K = 318.15</i>			
0.0202	0.99187	0.6047	113.26
0.0364	0.99288	0.6076	113.35
0.0529	0.99389	0.6118	113.43
0.0695	0.99490	0.6159	113.51
0.0862	0.99590	0.6224	113.64
0.1031	0.99689	0.6270	113.85
<hr/>			
<i>0.015^a</i>			
<hr/>			
<i>T/K = 298.15</i>			
0.0202	0.99888	0.9057	112.41
0.0364	0.99990	0.9122	112.44
0.0529	1.00091	0.9188	112.70
0.0694	1.00193	0.9243	112.72
0.0862	1.00294	0.9309	112.81
0.1031	1.00395	0.9377	112.9
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<i>T/K = 308.15</i>			
0.0202	0.99584	0.7312	113.56

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0.0364	0.99684	0.7365	113.71
0.0529	0.99784	0.7418	113.81
0.0694	0.99884	0.7483	113.91
0.0862	0.99983	0.7537	114.04
0.1031	1.00081	0.7583	114.25
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<i>T/K = 318.15</i>			
0.0202	0.99202	0.6071	115.28
0.0364	0.99300	0.6112	115.31
0.0529	0.99398	0.6165	115.37
0.0694	0.99496	0.6206	115.44
0.0862	0.99594	0.6259	115.44
0.1031	0.99691	0.6306	115.56
<hr/>			
0.020 ^a			
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<i>T/K = 298.15</i>			
0.0201	0.99899	0.9080	112.91
0.0364	1.00000	0.9146	112.99
0.0528	1.00101	0.9212	113.08
0.0694	1.00202	0.9278	113.16
0.0862	1.00302	0.9344	113.28
0.1031	1.00403	0.9401	113.29
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<i>T/K = 308.15</i>			
0.0201	0.99595	0.7335	114.04
0.0364	0.99694	0.7389	114.26
0.0528	0.99793	0.7453	114.39
0.0694	0.99892	0.7507	114.49
0.0862	0.99991	0.7572	114.51
0.1031	1.0009	0.7618	114.55
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T/K = 318.15			
0.0201	0.99216	0.6095	116.28
0.0364	0.99312	0.6136	116.43
0.0528	0.99408	0.6189	116.53
0.0694	0.99504	0.6242	116.62
0.0862	0.99600	0.6294	116.63
0.1031	0.99696	0.6341	116.66

^a Molality of TBAHS in aqueous solutions.

where M is the molar mass of L-ascorbic acid, m is the molality of 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 4.2 shows that apparent molar volumes (ϕ_V) increase with increasing temperature and TBAHS-content in the solutions under study. Such trends indicate that the interactions between solute and solvent as well as those between solute-solute or solute-cosolute change with temperature and solvent compositions. However, more information regarding solute-solute or solute-solvent interactions can be had from limiting apparent molar volumes at infinite dilution or standard partial molar volumes (ϕ_V^0) of the solute. As the plots of ϕ_V against square root of molal concentration (\sqrt{m}) were linear in the studied concentration range of L-ascorbic acid at all experimental temperatures, standard partial molar volume (ϕ_V^0) were obtained from the Masson equation [18]:

$$\phi_V = \phi_V^0 + S_V^* \sqrt{m} \quad (2)$$

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 coefficients (R^2) were within the range 0.91423-0.99541. The weighing factors were set equal to the inverse of variances 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 or ion-solvent interactions.

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Table 4.3. Partial molar volumes (ϕ_V^0) and the slopes (S_V^*) of Eq. 2 for L-ascorbic acid in different aqueous TBAHS solutions with corresponding standard deviations at different temperatures

T/K	$\frac{\phi_V^0 \times 10^6}{\text{m}^3 \cdot \text{mol}^{-1}}$	$\frac{S_V^* \times 10^6}{\text{m}^3 \cdot \text{kg}^{1/2} \cdot \text{mol}^{-3/2}}$	$\frac{\sigma \times 10^6}{\text{m}^3 \cdot \text{mol}^{-1}}$
0.000 ^a			
298.15	108.20 (±0.05)	5.05 (±0.19)	0.03
308.15	108.80 (±0.08)	8.28 (±0.32)	0.05
318.15	110.54 (±0.10)	8.89 (±0.40)	0.06
0.005 ^a			
298.15	108.67 (±0.05)	5.25 (±0.20)	0.03
308.15	109.69 (±0.06)	6.33 (±0.25)	0.04
318.15	111.57 (±0.06)	4.80 (±0.25)	0.04
0.010 ^a			
298.15	110.36 (±0.08)	3.68 (±0.33)	0.05
308.15	111.01 (±0.02)	3.86 (±0.10)	0.02
318.15	112.76 (±0.10)	3.14 (±0.39)	0.06

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0.015 ^a			
298.15	111.97 (±0.07)	2.93 (±0.30)	0.05
308.15	113.01 (±0.08)	3.63 (±0.33)	0.05
318.15	115.04 (±0.05)	1.50 (±0.19)	0.03
0.020 ^a			
298.15	112.56 (±0.04)	2.35 (±0.15)	0.02
308.15	113.72 (±0.06)	2.75 (±0.26)	0.04
318.15	116.01 (±0.05)	2.18 (±0.20)	0.03

^a Molality of TBAHS in aqueous solutions in mol · kg⁻¹. Standard errors are given in parenthesis.

The slope S_V^* provides information regarding solute-solute or ion-ion interactions. The values of ϕ_V^0 and S_V^* along with standard deviations (σ) for L-ascorbic acid in different aqueous TBAHS solutions at the experimental temperatures are reported in Table 4.3.

Although L-ascorbic acid contains four –OH groups at positions 2, 3, 5 and 6, the –OH groups at positions 2 and 3 are only acidic ($pK_a = 4.2$ and 11.6 at 298.15 K, respectively; other –OH groups remain as alcoholic residues [19]). Again, HSO_4^- ion readily achieves the equilibrium: $HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$ in aqueous solution at low temperatures (<373 K) under ambient pressure [20-22] and therefore within the pH range of the experimental solutions (pH = 2.29, 2.40, 2.48 and 2.60, respectively for the solutions with $m_{TBAHS} = 0.020, 0.015, 0.010$ and 0.005 mol · kg⁻¹), L-ascorbic acid can release only one proton (from position 2) in aqueous solutions studied and L-ascorbic acid behaves as a weak electrolyte. Anyway, our results (Table 4.3) shows

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that ϕ_V^0 values are positive and increase when both the experimental temperatures and TBAHS content in the solvents increase. This trend in ϕ_V^0 values indicates the presence of strong solute-solvent interactions and such interactions further strengthen at elevated temperatures and with higher concentrations of TBAHS in the ternary solutions. Such a trend in ϕ_V^0 values is at par the trends in ϕ_V values (as listed in Table 4.3) for the studied solutions. These facts may be attributed to increase in solvation of the ions at elevated temperatures [23]. Dependence of ϕ_V^0 values on the solvent composition is depicted in Fig. 4.2.

The parameter S_V^* is a volumetric coefficient that characterizes pair-wise interaction between the solvated species or ion-ion interaction in solution phase [24]. Its sign is determined by the interactions between the solute species.

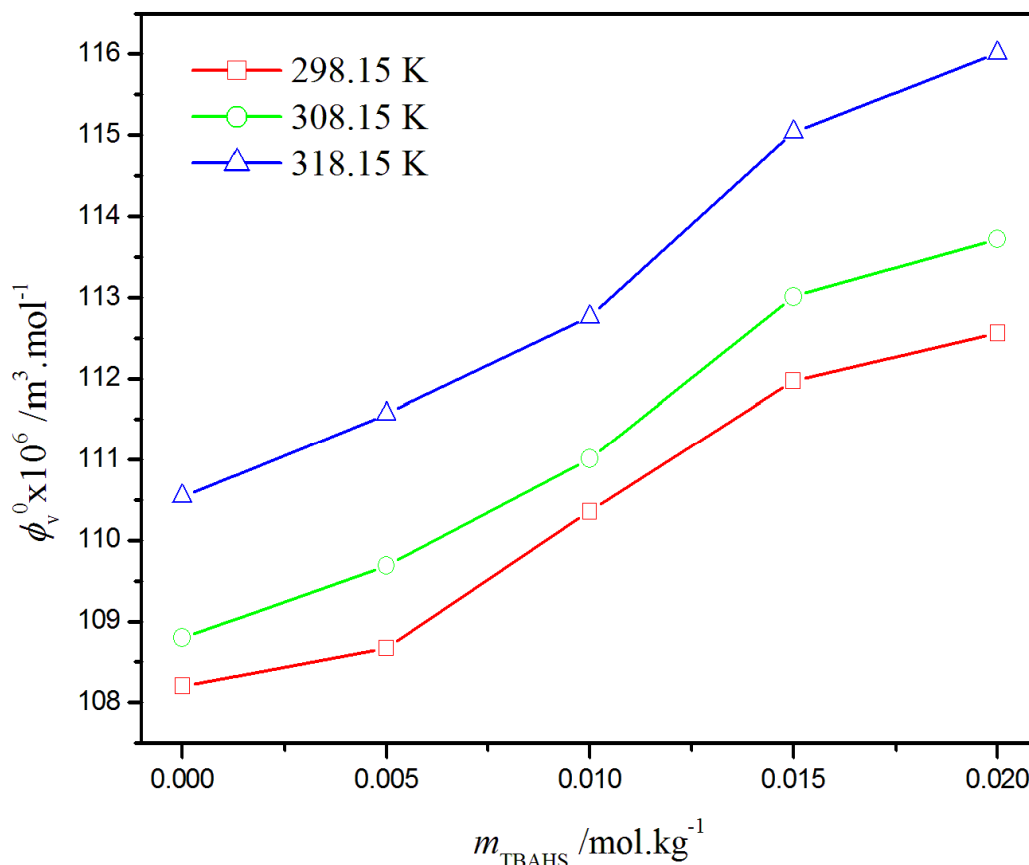


Fig. 4.2. Dependence of standard partial molar volumes (ϕ_V^0) for L-ascorbic acid on the molality of TBAHS (m_{TBAHS}) in aqueous solutions at $T = (298.15\text{-}318.15)$ K.

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In the present study, S_V^* values were found to positive for all the studied solutions. For ionic species like TBAHS and L-ascorbic acid 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 or ions [25] and such interactions probably diminishes with increasing molality of TBAHS due to solvent induced cosphere overlap or solute-solute hydrophobic interactions [23]. 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 or ion-solvent interactions play a dominant role over the solute-solute or ion-ion interactions in characterizing the volumetric properties of studied systems.

4.3.2. Standard transfer volumes

Limiting thermodynamic transfer properties provide information about the solute-cosolute interaction, because at infinite dilution 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:

$$\Delta_t\phi_V^0 = \phi_V^0[\text{Ascorbic acid} + \text{water} + \text{TBAHS}] - \phi_V^0[\text{Ascorbic acid} + \text{water}] \quad (3)$$

The $\Delta_t\phi_V^0$ values are depicted in Fig. 4.3 as a function of molality of TBAHS in the aqueous solutions. $\Delta_t\phi_V^0$ values are positive at all the experimental temperatures and increases monotonically with the increase in TBAHS content in ternary solutions. According to the cosphere overlap model, as developed by Friedman and Krishnan [26], the overlap of hydration cospheres of two ionic species results in an increase in volume but that of hydration cospheres of hydrophobic-hydrophobic and ion-hydrophobic groups results in volume decrease. The positive $\Delta_t\phi_V^0$ values indicate that ion-hydrophilic and hydrophilic-hydrophilic group interactions predominate over ion-hydrophobic, hydrophobic-hydrophobic and hydrophilic-hydrophobic interactions and the overall effect of the overlap of the hydration cospheres of L-ascorbic acid and TBAHS reduces the electrostriction of water by L-ascorbic acid. Such reduced

electrostriction results in a concomitant increase in volume and this effect further increase with increasing molality of TBAHS in the ternary solutions increase.

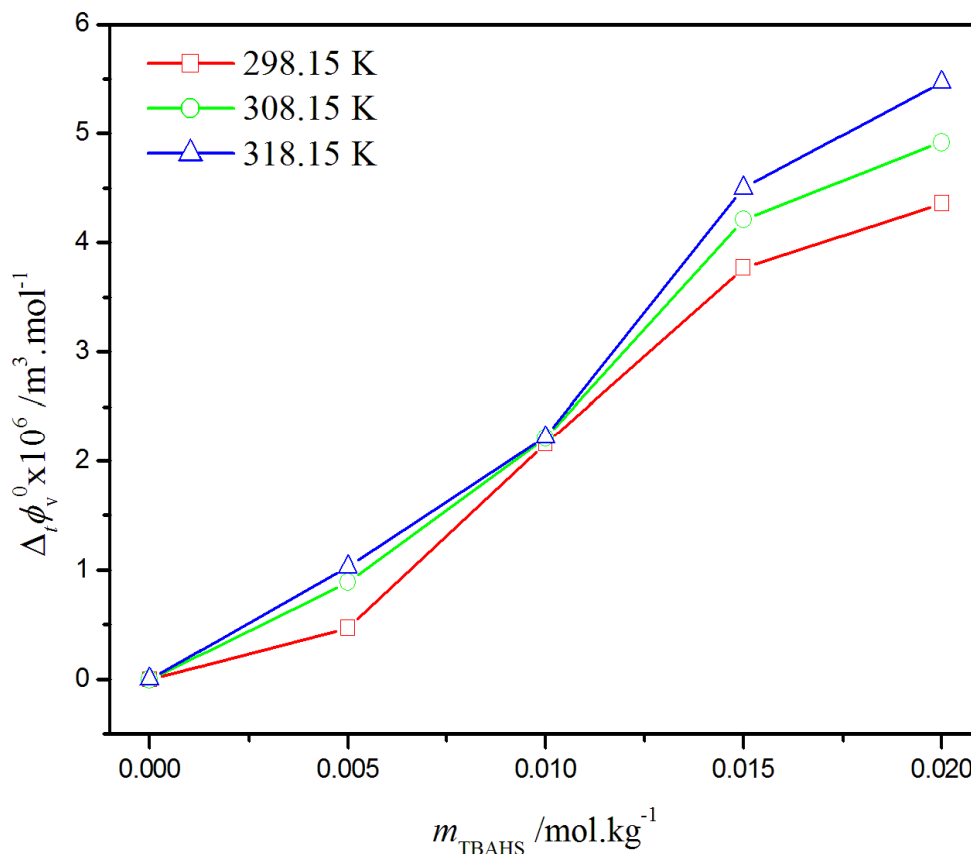


Fig. 4.3. Plots of standard partial molar volume of transfer ($\Delta_t \phi_V^0$) for L-ascorbic acid on the molality of TBAHS (m_{TBAHS}) in aqueous solutions at $T = (298.15-318.15)$ K.

4.3.3. Apparent molar expansibilities

Apparent molar volumes (ϕ_V) and densities (ρ) were further used to calculate the apparent molar expansibilities (ϕ_E) of L-ascorbic acid solutions by using the relation [17]:

$$\phi_E = \alpha \phi_V + \frac{1000(\alpha - \alpha_1)}{m \rho_1} \quad (4)$$

where α and α_1 are the coefficients of isobaric thermal expansion of the solution and solvent, 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

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coefficients of isobaric thermal expansion was $\pm 2.2 \cdot 10^{-5} \text{K}^{-1}$ 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 [18]:

$$\phi_E = \phi_E^0 + S_E \sqrt{m} \quad (5)$$

$(\partial \phi_E^0 / \partial T)_p$ values were obtained from the slope of a linear fit of ϕ_E^0 values (a least squares linear regression was used) against experimental temperature (T) with the correlation coefficient (R^2) values within the range 0.88448-0.95639. The ϕ_E^0 values are an important indicator of solute-solvent interactions and helps in interpretation of the long-range structure making or breaking properties of solutes [28]. The ϕ_E^0 values along with corresponding errors for different experimental solutions at different temperatures are given in Table 4.4. It reveals that ϕ_E^0 values are positive and further increase at higher temperatures. Such a trend in ϕ_E^0 values can be ascribed to the structural perturbation influenced by the gradual appearance of ‘caging effect’ or ‘packing effect’ [29] for L-ascorbic acid in the studied solutions and it does not behave like common electrolytes rather as a weak electrolyte and has hydrophobic character [23, 30]. According to Hepler [29] if the term $(\partial \phi_E^0 / \partial T)_p$ is positive, the solute is a structure maker otherwise it is a structure breaker. The $(\partial \phi_E^0 / \partial T)_p$ values for different ternary solutions are given in Table 4.4.

It shows that the $(\partial \phi_E^0 / \partial T)_p$ values are positive for all the studied solutions. Thus L-ascorbic acid seems to act a net structure maker in aqueous TBAHS solutions and the studied systems are characterized by the predominance of hydrophobic hydration over the electrostriction of water by the solute and cosolute molecules [29], *i.e.*, some of the electrostricted water molecules in the hydration spheres of the solute, cosolute or their constituents ions get released in favour of the normal bulk structure of water upon overlap of the cospheres resulting in volume increase in coexistence of the solute and cosolute.

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Table 4.4. Partial molar expansibilities (ϕ_E^0), its temperature dependence ($\partial\phi_E^0/\partial T$)_p and the slopes (S_E) of Eq. 5 for L-ascorbic acid in aqueous TBAHS solutions at $T = 298.15$ to 318.15 K.

Solvent	$\frac{\phi_E^0 \cdot 10^{-5}}{\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}$			$\frac{S_E \cdot 10^{-5}}{\text{m}^3 \cdot \text{kg}^{1/2} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}$			$\left(\frac{\partial\phi_E^0}{\partial T}\right)_p \cdot 10^{-8}$
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K	$\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$
0.000 ^a	7.95	8.00	8.11	1.80	1.83	1.84	8.14
	(±0.06)	(±0.07)	(±0.07)	(±0.03)	(±0.03)	(±0.03)	(±0.08)
0.005 ^a	10.63	10.72	10.85	-2.92	-2.90	-2.97	11.01
	(±0.05)	(±0.05)	(±0.05)	(±0.02)	(±0.02)	(±0.02)	(±0.08)
0.010 ^a	8.13	8.19	8.30	-3.18	-3.20	-3.25	8.43
	(±0.09)	(±0.09)	(±0.09)	(±0.04)	(±0.04)	(±0.04)	(±0.08)
0.015 ^a	11.42	11.52	11.66	-0.76	-0.77	-0.78	11.83
	(±0.04)	(±0.04)	(±0.04)	(±0.02)	(±0.02)	(±0.02)	(±0.08)
0.020 ^a	13.30	13.41	13.57	-0.16	-0.16	-0.16	13.64
	(±0.04)	(±0.04)	(±0.04)	(±0.01)	(±0.02)	(±0.02)	(±0.09)

^a Molality of TBAHS in aqueous solutions in $\text{mol} \cdot \text{kg}^{-1}$. Standard errors are given in parenthesis.

4.3.4. Viscometric results.

As L-ascorbic acid behaves as a weak electrolyte, solution viscosities were analyzed with the modified Jones-Dole equation [31]:

$$\eta_r = 1 + Bc \quad (6)$$

where $\eta_r = \eta/\eta_1$; η_1 , η and c stand for the solvent viscosity, the solution viscosity and molarity of L-ascorbic acid in the studied solutions, respectively. The viscosity B -coefficients were estimated by a weighted least squares linear regression of Eq. 6 with the correlation coefficients (R^2) within the range 0.99828-0.99912. The weighing factors were set equal to the inverse of variances of the η_r values for each data point. Viscosity B -coefficient gives a measure of structural modifications induced by solute-

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solvent or ion-solvent interactions [32]. Table 4.5 shows that the viscosity B -coefficients are positive and such values increase as both the amount of TBAHS in the ternary solution and the experimental temperature increase. These results suggest strong solute-solvent interactions in the ternary solutions and net structural enhancement at higher concentration of TBAHS at higher temperatures. Such interactions are also well reflected by the increase in solution viscosities induced by increasing the TBAHS concentration in the ternary solutions.

Table 4.5. Viscosity B -coefficient of L-ascorbic acid with the correlation coefficients (R^2), standard deviations (σ) for linear regression of Eq. 6 along with the solvation number (S_n) in aqueous TBAHS solutions at $T = (298.15 \text{ to } 318.15) \text{ K}$.

Parameters	298.15 K	308.15 K	318.15 K
		0.000 ^a	
$B \times 10^3$	0.417	0.431	0.452
$\text{m}^3 \cdot \text{mol}^{-1}$	(± 0.009)	(± 0.010)	(± 0.011)
R^2	0.99806	0.99841	0.99915
σ	0.002	0.002	0.001
S_n	3.85	3.96	4.09
	(± 0.01)	(± 0.03)	(± 0.03)
		0.005 ^a	
$B \times 10^3$	0.428	0.442	0.462
$\text{m}^3 \cdot \text{mol}^{-1}$	(± 0.012)	(± 0.021)	(± 0.023)
R^2	0.99800	0.99853	0.99883
σ	0.002	0.004	0.003
S_n	3.93	4.03	4.14
	(± 0.02)	(± 0.01)	(± 0.03)
		0.010 ^a	
$B \times 10^3$	0.440	0.463	0.489
$\text{m}^3 \cdot \text{mol}^{-1}$	(± 0.009)	(± 0.012)	(± 0.028)
R^2	0.99812	0.99854	0.99854
σ	0.002	0.002	0.005

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S_n	3.99	4.17	4.33
	(±0.03)	(±0.03)	(±0.02)
0.015 ^a			
$\frac{B \times 10^3}{\text{m}^3 \cdot \text{mol}^{-1}}$	0.450	0.489	0.502
	(±0.009)	(±0.015)	(±0.013)
R^2	0.99864	0.99894	0.99845
σ	0.002	0.003	0.002
S_n	4.02	4.29	4.36
	(±0.01)	(±0.02)	(±0.02)
0.020 ^a			
$\frac{B \times 10^3}{\text{m}^3 \cdot \text{mol}^{-1}}$	0.458	0.503	0.529
	(±0.009)	(±0.017)	(±0.014)
R^2	0.99888	0.99901	0.99904
σ	0.002	0.002	0.001
S_n	4.07	4.42	4.56
	(±0.02)	(±0.01)	(±0.02)

^a Molality of TBAHS in aqueous solutions in $\text{mol} \cdot \text{kg}^{-1}$.

Standard errors are given the parenthesis.

We have also calculated solvation or hydration numbers (S_n) for L-ascorbic acid using the relation [33]: $S_n = B/\phi_V^0$. 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 [33] and higher S_n values indicate solvated solutes with primary solvation sphere. S_n values as given in Table 4.5 suggest that L-ascorbic acid or its constituent ions remain solvated with primary solvation spheres in the aqueous solutions studied here and higher temperature favours solvations of L-ascorbic acid or its constituent ions 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 L-ascorbic acid from water to aqueous TBAHS solutions were determined by using the relation:

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$$\Delta_t B = B[\text{Ascorbic acid} + \text{water} + \text{TBAHS}] - B[\text{Ascorbic acid} + \text{water}] \quad (7)$$

The $\Delta_t B$ values are depicted in Fig. 4.4 as a function of TBAHS-molality in aqueous solutions and simply concur with the trends of solute-cosolute interactions reflected by $\Delta_t \phi_V^0$ values.

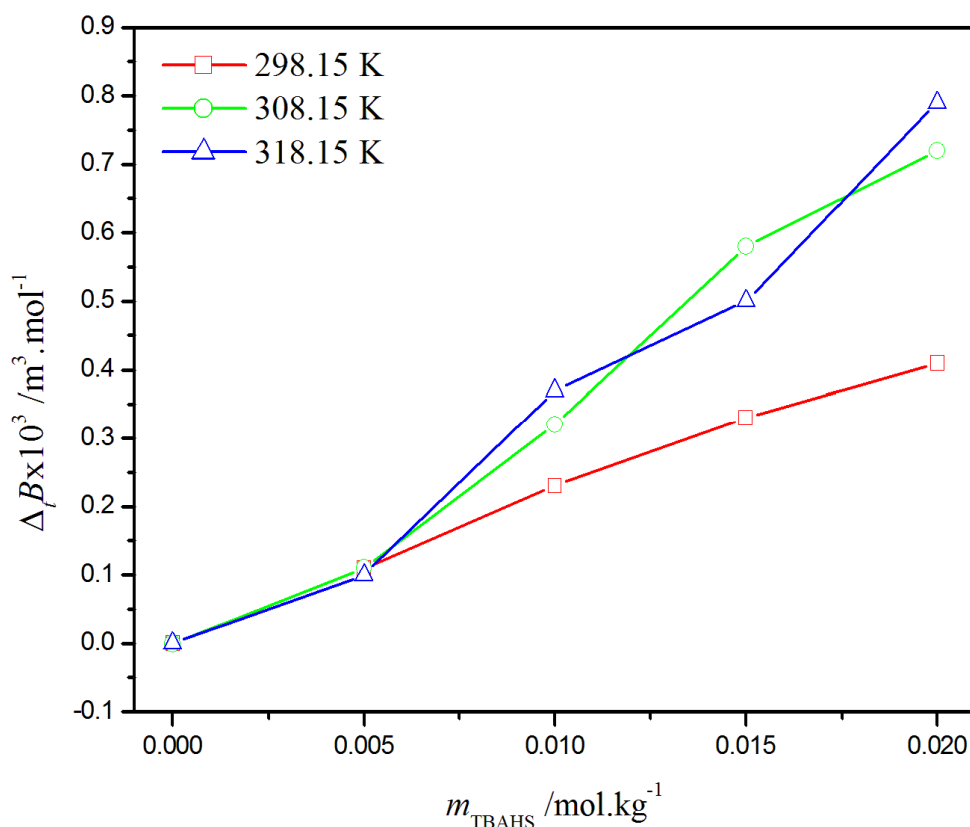


Fig. 4.4. Plots of viscosity B -coefficients of transfer ($\Delta_t B$) for L-ascorbic acid on the molality of TBAHS (m_{TBAHS}) in aqueous solutions at $T = (298.15-318.15)$ K.

4.3.5. Thermodynamics of viscous flow

According to Feakin's transition state theory of relative viscosity [32], the free energy of activation of viscous flow per mole of the solute ($\Delta\mu_2^{0\neq}$) is given by the relation:

$$\Delta\mu_2^{0\neq} = \Delta\mu_1^{0\neq} + RT(1000B + \phi_{V,2}^0 - \phi_{V,1}^0) / \phi_{V,1}^0 \quad (8)$$

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where $\phi_{V,1}^0$ and $\phi_{V,2}^0$ are the partial molar volumes of the solvent and solute, respectively. The free energy of activation of viscous flow for the solvent per mole ($\Delta\mu_1^{0\neq}$) is given by the relation [34]:

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT \ln(\eta_1 \phi_{V,1}^0 / h N_A) \quad (9)$$

where N_A is the Avogadro's number and the other symbols have their usual significance. The entropy of activation for ternary solutions ($\Delta S_2^{0\neq}$) were obtained from the negative slope of the plots of $\Delta\mu_2^{0\neq}$ against T ,

$$\Delta S_2^{0\neq} = -d(\Delta\mu_2^{0\neq})/dT \quad (10)$$

and the activation enthalpy ($\Delta H_2^{0\neq}$) has been calculated using the relation:

$$\Delta H_2^{0\neq} = \Delta\mu_2^{0\neq} + T\Delta S_2^{0\neq} \quad (11)$$

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 reported in Table 4.6. It shows that $\Delta\mu_1^{0\neq}$ is almost invariant of the solvent compositions and temperatures, implying that $\Delta\mu_2^{0\neq}$ is dependent mainly on the viscosity B -coefficients and ($\phi_{V,2}^0 - \phi_{V,1}^0$) terms. The $\Delta\mu_2^{0\neq}$ values contain the change in the free energy of activation of solvent molecules in presence of solute as well as the contribution from the movement of solute molecules or ions. $\Delta\mu_2^{0\neq}$ values were positive and greater than $\Delta\mu_1^{0\neq}$ values at all the experimental temperatures for all the aqueous solutions suggesting that solute (ion)-solvent interactions are stronger in the ground state than in the transition state and in the transition state, the solvation of the solute (ions) is less favoured energetically. According to Feakins *et al.* [32], the fact that $\Delta\mu_2^{0\neq} > \Delta\mu_1^{0\neq}$ for solutes with positive viscosity B -coefficients indicates stronger solute-solvent interactions; thereby suggesting the formation of transition state to be accompanied by the rupture and distortion of the intermolecular forces in solvent structure.

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Table 4.6. Values of $\phi_{V,2}^0 - \phi_{V,1}^0$, $\Delta\mu_1^{0\#}$, $\Delta\mu_2^{0\#}$, $T\Delta S_2^{0\#}$, $\Delta H_2^{0\#}$ for L-ascorbic acid in aqueous TBAHS solutions at different temperatures

Parameters	298.15 K	308.15 K	318.15 K
0.000 ^a			
$\frac{(\phi_{V,2}^0 - \phi_{V,1}^0) \times 10^6}{\text{m}^3 \cdot \text{mol}^{-1}}$	90.08	90.57	92.17
$\frac{\Delta\mu_1^{0\#}}{\text{kJ} \cdot \text{mol}^{-1}}$	9.17 (±0.01)	8.95 (±0.01)	8.76 (±0.02)
$\frac{\Delta\mu_2^{0\#}}{\text{kJ} \cdot \text{mol}^{-1}}$	78.53 (±0.15)	82.25 (±0.17)	87.12 (±0.15)
$\frac{T\Delta S_2^{0\#}}{\text{kJ} \cdot \text{mol}^{-1}}$	-128.12 (±0.79)	-132.42 (±0.85)	-136.72 (±0.97)
$\frac{\Delta H_2^{0\#}}{\text{kJ} \cdot \text{mol}^{-1}}$	-49.60 (±0.29)	-50.17 (±0.32)	-49.60 (±0.25)
0.005 ^a			
$\frac{(\phi_{V,2}^0 - \phi_{V,1}^0) \times 10^6}{\text{m}^3 \cdot \text{mol}^{-1}}$	90.52	91.39	93.19
$\frac{\Delta\mu_1^{0\#}}{\text{kJ} \cdot \text{mol}^{-1}}$	9.18 (±0.02)	8.97 (±0.01)	8.79 (±0.01)
$\frac{\Delta\mu_2^{0\#}}{\text{kJ} \cdot \text{mol}^{-1}}$	80.0 (±0.15)	83.62 (±0.13)	88.70 (±0.13)
$\frac{T\Delta S_2^{0\#}}{\text{kJ} \cdot \text{mol}^{-1}}$	-129.71 (±0.52)	-134.06 (±0.52)	-138.41 (±0.54)
$\frac{\Delta H_2^{0\#}}{\text{kJ} \cdot \text{mol}^{-1}}$	-49.71 (±0.29)	-50.44 (±0.31)	-49.71 (±0.27)
0.010 ^a			
$\frac{(\phi_{V,2}^0 - \phi_{V,1}^0) \times 10^6}{\text{m}^3 \cdot \text{mol}^{-1}}$	92.21	92.71	94.29

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$\frac{\Delta\mu_1^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	9.19	8.98	8.80
	(±0.02)	(±0.01)	(±0.02)
$\frac{\Delta\mu_2^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	81.89	86.77	92.32
	(±0.29)	(±0.38)	(±0.25)
$\frac{T\Delta S_2^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	-155.50	-160.72	-165.93
	(±0.79)	(±0.78)	(±0.79)
$\frac{\Delta H_2^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	-73.61	-73.95	-73.61
	(±0.44)	(±0.44)	(±0.41)
0.015 ^a			
$\frac{(\phi_{V,2}^0 - \phi_{V,1}^0) \times 10^6}{\text{m}^3 \cdot \text{mol}^{-1}}$	93.73	94.71	96.57
$\frac{\Delta\mu_1^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	9.21	8.98	8.82
	(±0.04)	(±0.04)	(±0.05)
$\frac{\Delta\mu_2^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	83.09	90.15	94.54
	(±0.17)	(±0.17)	(±0.16)
$\frac{T\Delta S_2^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	-170.66	-176.39	-182.11
	(±0.75)	(±0.75)	(±0.78)
$\frac{\Delta H_2^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	-87.57	-86.24	-87.57
	(±0.56)	(±0.58)	(±0.58)
0.020 ^a			
$\frac{(\phi_{V,2}^0 - \phi_{V,1}^0) \times 10^6}{\text{m}^3 \cdot \text{mol}^{-1}}$	94.32	95.42	97.54
$\frac{\Delta\mu_1^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	9.22	9.00	8.83
	(±0.04)	(±0.04)	(±0.05)
$\frac{\Delta\mu_2^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	84.27	92.79	98.57
	(±0.17)	(±0.18)	(±0.17)

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$\frac{T\Delta S_2^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	-213.10 (± 0.96)	-220.25 (± 0.96)	-227.40 (± 0.98)
$\frac{\Delta H_2^{0\neq}}{\text{kJ} \cdot \text{mol}^{-1}}$	-128.83 (± 0.37)	-127.46 (± 0.35)	-128.83 (± 0.38)

^a Molality of TBAHS in aqueous solutions in $\text{mol} \cdot \text{kg}^{-1}$.

Standard errors are given the parenthesis.

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 L-ascorbic acid in the studied solutions suggest it to be a net structure promoter/maker. However, negative $\Delta S_2^{0\neq}$ and $\Delta H_2^{0\neq}$ values suggest that the transition state is associated with bond formation (between solute-solvent components) resulting in the decrease in order and the viscous flow is exothermic.

4.4. Conclusion

In summary, different derived parameters like ϕ_V^0 and viscosity B -coefficients for the solutions of L-ascorbic acid in the aqueous solvent systems indicated that the studied solutions are predominantly characterized by solute (ion)-solvent interactions rather than by solute-solute or ion-ion interactions and the L-ascorbic acid acts as a net structure promoter for the studied solutions. S_n values indicated that the L-ascorbic acid or its constituent ions remain solvated with primary solvation spheres in the aqueous solvent systems investigated.

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