CHAPTER-D

D.1: Apparent molar volume, Viscosity *B*-coefficient and Adiabatic Compressibility of Tetrabutylammonium bromide in aqueous Ascorbic acid Solutions at T = (298.15, 308.15 and 318.15) K

D.1.1. Introduction

Tetraalkyl ammonium salts are bulky in nature and are known to orient water molecules around them depending on their alkyl chain[1-2]. Salts like tetrabutyl ammonium bromide (TBAB) can give a better insight into the effect of electrostatic and hydrophobic interactions on the stability of vitamins as these salts are known to influence macromolecular conformations by weakening attraction or repulsion inter and intra charge-charge interactions and by affecting hydrophobic interactions through the side chain of the alkyl groups.

Enzymes are the functional unit of cell metabolism as they catalyze different reactions to degrade nutrient molecules into simpler ones. Many enzymes require a non-protein cofactor for their catalytic activities. Vitamins are essential precursors for various coenzymes. These coenzymes are therefore required in almost metabolic pathways[3].The most prominent role of vitamin C (ascorbic acid) is its immune-stimulating effect e.g. important for defense against infections such as common colds. It also acts as an inhibitor of histamine a compound that is released during allergic reactions. As a powerful antioxidant it can neutralize pollutants and toxins. Thus it is able to prevent the formation of potentially carcinogenic nitrosamines in the stomach. Importantly vitamin C is also able to regenerate other antioxidants as vitamin E. Vitamin C is required for the synthesis of collagen, the intercellular "cement" which gives the structure of muscles, vascular tissues, bones, and tendon. Vitamin C with Zn is also important for the healing of wounds. It is also needed for the metabolism of bile acids which may have implications for blood cholesterol levels and gallstones. Vitamin C plays an important role for the synthesis of several important peptide hormones neurotransmitters and creatinine. It also enhances the eye's ability and delay the progression of advanced age related muscular degeneration.

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The extensive studies on partial molar volumes and viscosity B- coefficients of TBAB[4] in aqueous salt solutions are rare. Since partial molar volume and viscosity B-coefficients of a solute reflects the cumulative effects[5-6] of the solute-solute and solute-solvent interactions. In this paper we have attempted to study these properties for tetrabutylammonium bromide (TBAB) in aqueous binary mixture of ascorbic acid at T= (298.15, 308.15 and 318.15) K to understand the various interactions existing in the ternary systems under investigation.

D.1.2. Experimental Section

Ascorbic acid was purchased from Sd. Fine chemical Limited, and used as delivered. Its mass purity, as supplied, is 98 %. TBAB was purchased from Thomas Baker (Chemicals), Limited Mumbai .The TBAB was purified by dissolving it in mixed alcohol medium and recrystallising from the solvent ether medium[4]. After filtration, the salt was dried in vacuo for few hours. Ascorbic acid was recrystallised twice from aqueous ethanol solution and dried under vacuum at T=348 K for 6 hr. Thereafter, they were stored over P_2O_5 in a desiccator before use[7]. Triply distilled water with a specific conductance $<10^{-6}$ $S{\cdot}cm^{-1}$ was used for the preparation of different aqueous ascorbic acid solutions. The physical properties of different aqueous ascorbic acid solutions are listed in table 1.

Stock solutions of TBAB in different aqueous ascorbic acid solutions were prepared by mass, and the working solutions were prepared by mass dilution. The conversion of molality into molarity was accomplished using experimental density values. All solutions were prepared afresh before use. The uncertainty in the molarity of the TBAB solutions was evaluated to be 0.0001 $mol{\cdot}dm^{-3}$

The densities were measured with an Ostwald–Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at T = (298.15, 308.15, and 318.15) K with doubly distilled water and benzene. The pycnometer with the test solution was equilibrated in a water bath maintained at ± 0.01 K of the desired temperatures. The pycnometer was then removed from the thermostatic bath, properly dried, and weighed. Adequate precautions were taken to avoid evaporation losses during the course of actual measurements. The mass measurements, accurate to ± 0.01 mg, were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The total uncertainty in density was estimated to be 0.0002 $g{\cdot}cm^{-3}$, and that of the temperature is 0.01 K.

The viscosity was measured by means of a suspended Ubbelohde type viscometer thoroughly cleaned, dried, and calibrated at T = (298.15, 308.15, and 318.15) K with triply distilled water and purified methanol. It was filled with experimental liquid and placed vertically in a glass-sided thermostat maintained constant to 0.01 K. After attainment of thermal equilibrium, the efflux times of flow of liquids were recorded with a stopwatch correct to ± 0.1 s. The viscosity of the solution, η, is given by the following equation:

$$\eta = \left(kt - \frac{l}{t}\right)\rho \tag{1}$$

where k and l are the viscometer constants and t and ρ are the efflux time of flow (in seconds) and the density of the experimental liquid, respectively. The uncertainty in viscosity measurements was within 0.002 mPa·s. The ultrasonic speeds of sound for the solutions were determined by a multi-frequency ultrasonic interferometer (Mittal Enterprises, New Delhi, India) working at 2 MHz, calibrated with purified water and benzene at 298.15 K. The temperature stability was maintained within ±0.01 K by circulating thermostatic water around the cell with a circulating pump. The details of the methods and techniques have been described elsewhere[8-9]. The TBAB solutions studied here were prepared by mass, and the conversion of molality to molarity was accomplished[8-9].using experimental density values. The experimental values of concentrations (c), densities (ρ), viscosities (η) and derived parameters at various temperatures are reported in Table 2.

D.1.3. Results and Discussion

To study the solvation state of TBAB in aqueous ascorbic acid solutions and the interaction between TBAB and ascorbic acid, data for partial molar volumes are important. For this purpose, the apparent molar volumes (V_ϕ) were determined from the solution densities using the following equation[8-9] and were found similar with B.Das et al results[10]

$$V_\phi = \frac{M_2}{\rho_0} - \frac{1000}{c}\left(\frac{\rho - \rho_0}{\rho_0}\right) \tag{2}$$

Here M_2 is the molar mass of the solute, c is the molarity of the solution, ρ_0 and ρ are the densities of the solvent and solution, respectively. The plots of V_ϕ against the square root of molar concentration $c^{1/2}$, were non-linear and V_ϕ values were fitted to the following equation[11]:

$$V_\phi = V_\phi^0 + A_v c^{1/2} + B_v c \qquad (3)$$

where V_ϕ^0 is the partial molar volume at infinite dilution, and A_v and B_v are two adjustable parameters. The V_ϕ^0 values were calculated applying a least-squares technique to the plots of V_ϕ versas $c^{1/2}$ using Eq. 3. The values of V_ϕ^0, A_v; and B_v at each temperature are listed in Table 3. The estimated uncertainties in V_ϕ^0 values are represented by the standard deviation σ, which is equal to the root mean square of the deviation between the experimental and calculated V_ϕ for each data point. V_ϕ^0 values for the aqueous ascorbic acid solutions at (298.15 , 308.15, and 318.15) K were in good agreement with V_ϕ^0 values reported earlier[12] . Table 3 shows that V_ϕ^0 values are generally positive and increase with an increase in both the temperature and molarity of ascorbic acid in the solutions. This indicates the presence of strong solute–solvent interactions, and these interactions are further strengthened at higher temperatures and higher concentrations of ascorbic acid in the solutions. Ascorbic acid behaves as a vinylogous carboxylic acid where in the double bond transmits electron pairs between the hydroxyl group and the carbonyl[13]. There are two resonating structures for the deprotonated form, differing in the position of double bond. The deprotonated is an enolate which is usually strongly basic. Ascorbic acid also converts into two unstable diketone tautomers by proton transfer, although it is the most stable in the enol form. The proton of the enol is lost, and reacquired by electrons from the double bond to produce a diketone[14]. This is an enol reaction. There are two possible forms: 1,2 diketone and 1,3 diketone. Their results revealed that ascorbic acid associates in aqueous solutions with the hydroxyl groups of each ascorbic acid molecule creating large associated species at higher concentrations. This behavior is consistent with the observed changes in the values of parameters A_v and B_v. This also manifests that the the effect of parameter A_v predominates over that of parameter B_v in characterizing V_ϕ values in equation (3).

The partial molar volumes V_ϕ^0 were fitted to a polynomial of the following type:

$$V_\phi^0 = a_0 + a_1 T + a_2 T^2 \tag{4}$$

Values of the coefficients a_0, a_1, a_2 of the above equation for different TBAB solutions are reported in Table 4.

The partial molar expansibilities ϕ_E^0can be obtained by the following equation[15]:

$$\phi_E^0 = \left(\frac{\delta V_\phi^0}{\delta T}\right)_P = a_1 + 2a_2 T \tag{5}$$

The values of ϕ_E^0 for different ternary solutions at T = (298.15, 308.15, and 318.15) K are given in Table 5. Table 5 shows that ϕ_E^0 values increase as the temperature increases.

According to Hepler[16], the sign of $\left(\frac{\delta \phi_E^0}{\delta T}\right)_P$ or $\left(\frac{\delta^2 V_\phi^0}{\delta T^2}\right)_P$ is a better criterion in characterizing the long-range structure-making and structure-breaking ability of the solutes in solution. The general thermodynamic expression is as follows:

$$\left(\frac{\delta \phi_E^0}{\delta T}\right)_P = \left(\frac{\delta^2 V_\phi^0}{\delta T^2}\right)_P = 2a_2 \tag{6}$$

If the sign of $\left(\frac{\delta \phi_E^0}{\delta T}\right)_P$ is positive, the solute is a structure maker, otherwise, it is a structure breaker. As evident from Table 5, TBAB predominantly acts as a structure maker, and its structure-making ability increases with an increase in both the temperature and molarity of ascorbic acid in the solutions. But its structure-making ability decreases some what at higher concentrations of ascorbic acid in the mixtures. This fact may be attributed to the gradual disappearance of the caging or packing effect[17] in ternary solutions. This observation is in line with the observation made by Kundu and Kishore[12]. It is suggested that TBAB acts as a water-structure promoter due to hydrophobic hydration. The small positive values of $\left(\frac{\delta \phi_E^0}{\delta T}\right)_P$ at (0.10 and 0.15) mol.dm^{-3} aqueous ascorbic acid solutions are probably due to higher structure promoting ability of ascorbic acid than TBAB with comparatively higher V_{ϕ}^{0} value in aqueous solution[2] originating from hydrophobic hydration with greater degree hydrogen bonding than the bulk water[18]

Partial molar volumes of transfer ΔV_{ϕ}^{0} from water to different aqueous ascorbic acid solutions have been determined using the relations[19-20],

$$\Delta V_{\phi}^{0} = V_{\phi}^{0} \text{ (aqueous ascorbic acid solutions) - } V_{\phi}^{0} \text{ (water)} \tag{7}$$

The ΔV_{ϕ}^{0} value is independent of solute–solute interactions and therefore provides information regarding solute–co solute interactions[19]. It can be seen from Table 7, that the value of V_{ϕ}^{0} is positive at all experimental temperatures and increases with the molarity of ascorbic acid in the ternary solutions. The concentration dependence of the thermodynamic properties of the solutes in aqueous solutions can be explained in terms of the overlap of hydration co-spheres. According to the co-sphere model, as developed by Friedman and Krishnan[21], the effect of overlap of the hydration co-spheres is destructive i.e., the overlap of hydration co-spheres of hydrophobic–hydrophobic groups results in a net volume decrease. However, in the present study, the positive values of ΔV_{ϕ}^{0} indicate that solute-solvent interactions are predominant and the overall effect of the overlap of the hydration co-spheres of TBAB and ascorbic acid reduce the effect of electrostriction of water by TBAB molecules, and this effect increases with the molarity of ascorbic acid in the ternary mixtures as shown in Fig.1 (ΔV_{ϕ}^{0} versus molarity of ascorbic acid in solution). In addition, standard partial molar volumes of the solute have also been explained by a simple model[22-23]:

$$V_{\phi}^{0} = V_{\text{VW}} + V_{\text{Void}} - V_{\text{S}} \tag{8}$$

where V_{VW} is the van der Waals volume, V_{Void} is the volume associated with voids or empty space, and V_{S} is the shrinkage volume due to electrostriction. Assuming that V_{VW} and V_{Void} have the same magnitudes in water and in aqueous ascorbic acid solutions for the same solute[24], the increase in V_{ϕ}^{0} values and the positive ΔV_{ϕ}^{0} values can be attributed to the decrease in the shrinkage volume of water by TBAB in the presence of ascorbic acid. This fact suggests that ascorbic acid has a dehydration effect on the hydrated TBAB.

In the literature[12], pyridine has been noted as a structure breaker in aqueous solutions, and the structure-promoting tendency of TBAB has been assigned to the Bu_4N^+ ion. Thus, the interactions between TBAB and ascorbic acid in water can roughly be summarized as follows: (i) interaction of Bu_4N^+ ion with the of –O-H group of ascorbic acid (ii) interaction of Bu_4N^+ ion of TBAB with the –O- atom of the cyclic ring of ascorbic acid , (iii) interaction of Bu_4N^+ ion of TBAB with the O-atom in the carboxylic acid group of ascorbic acid,(iv) interaction of Br^- ion with the H-atom of the –O-H group of ascorbic acid , and(v) ionic-hydrophobic interactions between ions TBAB and non polar part of ascorbic acid molecules, where interaction (i)-(iv) manifest positively, the factor (v) contribute negatively to V_ϕ^0 values Therefore, the overall positive V_ϕ^0 values indicate that solute-solvent interactions predominate over solvent-solvent interactions and thus reduce the electrostriction of water molecules by TBAB imparting positive values of ΔV_ϕ^0 .

The viscosity data of the aqueous and aqueous ascorbic acid solutions of TBAB have been analyzed using the Jones–Dole[25] equation,

$$\frac{(\eta/\eta_0-1)}{\sqrt{c}}=\frac{(\eta_r-1)}{\sqrt{c}}=A+B\sqrt{c} \tag{9}$$

where $\eta_r = \eta/\eta_0$, and η are the viscosities of the solvent and solution, respectively, and c is the molar concentration of a solution. *A* and *B* are the Jones-Dole constants estimated by a least-squares method and reported in Table 6.

Table 6 shows that the values of the *A* coeffcient are generally negative for all solution at the experimental temperatures. These results indicate the presence of weak solute–solute interactions, and these interactions further decrease with an increase in both the temperature and molarity of ascorbic acid in the mixtures.

The viscosity *B*-coefficient[26] reflects the effects of solute–solvent interactions on the solution viscosity. The viscosity *B*-coefficient is a valuable tool to provide information concerning the solvation of solutes and their effects on the structure of the solvent in the local vicinity of the solute molecules. Table 6 implies that the values of the viscosity *B*-coefficient for TBAB in the studied solvent systems are positive, thereby suggesting the presence of strong solute–solvent interactions and these types of interactions are strengthened with an increase in both the temperature and molarity of ascorbic acid in the mixtures.

Viscosity *B*-coefficients of transfer ΔB from water to different aqueous ascorbic acid solutions have been determined using the relations[19-20],

$$\Delta B = B(\text{aqueous ascorbic acid solution}) - B(\text{water}) \qquad (10)$$

The ΔB values shown in Table 7 and depicted graphically in Fig.1 (ΔB versus molarity of ascorbic acid in solution) as a function of molarity of ascorbic acid in solutions at the experimental temperatures support the results obtained from ΔV_ϕ^0 values discussed above.

The adiabatic compressibility (β) was evaluated from the following equation

$$\beta = \frac{1}{u^2 \rho} \qquad (11)$$

Where 'ρ' is the solution density and 'u' is the sound speed of the solution. The apparent molal adiabatic compressibility (K_ϕ) of the solution was determined from the relation

$$K_\phi = \frac{\beta M}{\rho_0} + \frac{1000(\beta \rho_0 - \beta_0 \rho)}{m \rho \rho_0} \qquad (12)$$

Where β_0, β are the adiabatic compressibility of the solvent & solution, respectively and m is molal concentration of the solution. In equation[12] molality (m) has been used rather than concentration (c), because molality is independent of temperature and we performed acoustic calculations only at 298.15 K. Limiting partial molal adiabatic compressibility (K_ϕ^0) and the experimental slopes (S_k^*) were obtained by fitting φ_k against the square root of molality ($\sqrt{m}$) using the method least squares

$$K_\phi = K_\phi^0 + S_k^* \sqrt{m} \qquad (13)$$

Values of m , u , β, K_ϕ, K_ϕ^0 and S_k^* are presented in table 9. A perusal of table 9 shows that the K_ϕ^0 values are positive except 0.00(M) and S_k^* values are negative for all the ternary solution. Since the values of K_ϕ^0 and S_k^* measures of ion-solvent & ion-ion interaction, the results are in good agreement with those drawn from the values V_ϕ^0 and S_V^* discussed earlier.

The viscosity data have also been analyzed on the basis of transition state theory for the relative viscosity of the solutions as suggested by Feakins et al.[27] using,

$$\Delta\mu_2^{0\neq} = \Delta\mu_1^{0\neq} + \frac{RT}{\bar{V}_1^0}(1000B + \bar{V}_2^0 - \bar{V}_1^0) \tag{14}$$

where the $\bar{V}_1^0$ and the $\bar{V}_2^0$ are the partial molar volumes of the solvent and solute respectively. $\Delta\mu_2^{0\neq}$ is the contribution per mole of the solute to the free energy of activation for the viscous flow of solutions have been determined from the above relation and $\Delta\mu_1^{0\neq}$ is the free energy of activation per mole of solvent mixture is calculated by the following relation[27]:

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT\ln(\frac{\eta_0\bar{V}_1^0}{hN_A}) \tag{15}$$

where *h* is Planck's constant, N_A is Avogadro's number and $\Delta G_1^{0\neq}$ is the free-energy of activation per-mole of solvent mixture. From Table-8, it is seen that $\Delta\mu_1^{0\neq}$ is almost constant at *all temperatures and solvent compositions. It implies that* $\Delta\mu_2^{0\neq}$ *is dependent mainly on the* values of viscosity *B*-coefficients and ($\bar{V}_2^0$ $-\bar{V}_1^0$) terms. $\Delta\mu_2^{0\neq}$ values were positive at all experimental temperatures indicates that the viscosity increases as the temperature and molarity of ascorbic acid increases. So the formation of the transition state becomes less favorable[27].

According to Feakins et al.[27], $\Delta\mu_2^{0\neq} > \Delta\mu_1^{0\neq}$ for solutes having positive viscosity *B*-coefficients indicates stronger solute-solvent interactions, suggesting the formation of a transition state which is accompanied by the rupture and distortion of the intermolecular forces in the solvent structure [27]. The larger is the value of $\Delta\mu_2^{0\neq}$, the greater is the structure -making tendency of the solute, and the positive values of $\Delta\mu_2^{0\neq}$ for TBAB in the different aqueous ascorbic acid solutions suggests TBAB is a net structure promoter in these ternary mixtures. Equation 16 has been used to calculate the entropy of activation ($\Delta S_2^{0\neq}$) for solutions, from the relation[27]

$$\Delta S_2^{0\neq} = -\frac{d(\Delta\mu_2^{0\neq})}{dT} \tag{16}$$

$\Delta S_2^{0\neq}$ has been calculated from the slope of the plots of $\Delta\mu_2^{0\neq}$ versus *T* by using a least -square treatment. The enthalpy of activation has been determined by using the following relation[27]:

$$\Delta H_2^{0\neq} = \Delta \mu_2^{0\neq} + T\Delta S_2^{0\neq} \tag{17}$$

The values of $\Delta \mu_2^{0\neq}$ and $\Delta H_2^{0\neq}$ are reported in Table 8. They are negative for all experimental solutions at all temperatures which suggest that the transition state is associated with bond formation and an increase in order.

D.1.4. Conclusion

In summary, ϕ_V^o and viscosity *B*-coefficient values for TBAB indicate the presence of strong solute–solvent interactions, and these interactions are further strengthened at higher temperatures and higher concentrations of ascorbic acid in ternary solutions. This study also reveals that TBAB acts as a water-structure promoter due to hydrophobic hydration in the presence of ascorbic acid and ascorbic acid has a dehydration effect on the hydrated TBAB.

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Table 1. Density ρ , and viscosity η , of different aqueous Ascorbic Acid solution at different temperatures

Aqueous Ascorbic Acid solution/ (mol·dm^{-3})	T/K	ρ/(g·cm^{-3})	η/ (mPa·s)
0.05	298.15	1.0006	0.8970
	308.15	0.9974	0.7299
	318.15	0.9934	0.5956
0.1	298.15	1.0042	0.8794
	308.15	1.0005	0.7121
	318.15	0.9968	0.6079
0.15	298.15	1.0072	0.9180
	308.15	1.0042	0.7381
	318.15	1.0003	0.6226

Table 2 Molarity c, density ρ, viscosity η, apparent molar volumes V_ϕ, and $(\eta_r - 1)/c^{1/2}$ for TBAB in different aqueous ascorbic acid solutions at different temperatures.

c/(mol· dm^{-3})	ρ / (g· cm^{-3})	η/ (mPa·s)	V_ϕ /(cm^3·mol^{-1})	(η_r - 1) / √C
		0.00^a		
		T=298.15 K		
0.0250	0.9977	0.904	296.64	0.0740
0.0450	0.9983	0.893	295.62	0.0885
0.0550	0.9986	0.898	294.78	0.0998
0.0650	0.9990	0.900	293.76	0.1021
0.0750	0.9993	0.905	292.86	0.1172
0.0850	0.9997	0.908	291.78	0.1224
		T=308.15 K		
0.0249	0.9947	0.733	298.44	0.0910
0.0449	0.9953	0.740	297.15	0.1147
0.0548	0.9956	0.743	296.57	0.1235
0.0648	0.9959	0.747	295.42	0.1356
0.0748	0.9963	0.752	294.31	0.1480
0.0847	0.9966	0.755	293.43	0.1560
		T=318.15 K		
0.0248	0.9908	0.605	301.33	0.0630
0.0447	0.9914	0.610	299.88	0.0860
0.0546	0.9917	0.612	299.14	0.0970
0.0646	0.9920	0.617	298.45	0.1170
0.0745	0.9923	0.619	297.29	0.1250
0.0844	0.9927	0.622	296.18	0.1360
		0.05^a		
		298.15 K		
0.0250	1.0012	0.914	299.93	0.1200
0.0450	1.0017	0.928	298.65	0.1630
0.0550	1.0020	0.936	297.81	0.1850
0.0650	1.0023	0.943	296.60	0.2026
0.0750	1.0026	0.949	295.63	0.2106
0.0850	1.0030	0.957	294.02	0.2285
		308.15 K		
0.0249	0.9979	0.738	302.17	0.0680
0.0449	0.9984	0.748	300.76	0.1180
0.0548	0.9986	0.755	299.85	0.1460
0.0648	0.9990	0.760	298.52	0.1643
0.0748	0.9993	0.765	297.36	0.1780
0.0847	0.9996	0.770	296.36	0.1876
		318.15 K		
0.0248	0.9938	0.599	308.00	0.0360

Table 2: (Continued)

c/(mol· dm^{-3})	ρ / (g· cm^{-3})	η/ (mPa·s)	V_ϕ /(cm^3·mol^{-1})	$(\eta_r - 1) / \sqrt{C}$
0.0447	0.9942	0.606	306.58	0.0860
0.0546	0.9944	0.609	305.80	0.0990
0.0646	0.9946	0.613	304.80	0.1168
0.0745	0.9949	0.619	303.84	0.1420
0.0844	0.9952	0.624	302.80	0.1660
		0.10^a		
		T=298.15 K		
0.0250	1.0046	0.907	306.04	0.1980
0.0450	1.0050	0.932	304.60	0.2800
0.0550	1.0052	0.942	303.53	0.3030
0.0650	1.0055	0.953	302.40	0.3280
0.0750	1.0057	0.963	301.39	0.3470
0.0850	1.0060	0.978	300.59	0.3850
		T=308.15 K		
0.0249	1.0009	0.735	307.54	0.2051
0.0449	1.0012	0.754	305.63	0.2800
0.0548	1.0015	0.763	304.40	0.3070
0.0648	1.0017	0.773	303.53	0.3340
0.0748	1.0020	0.782	302.56	0.3585
0.0847	1.0023	0.796	301.23	0.4050
		T=318.15 K		
0.0248	0.9972	0.632	310.32	0.2611
0.0447	0.9975	0.650	308.56	0.3274
0.0546	0.9977	0.658	307.46	0.3521
0.0646	0.9979	0.668	306.53	0.3902
0.0745	0.9981	0.678	305.83	0.4236
0.0844	0.9984	0.690	304.60	0.4651
		0.15^a		
		T=298.15 K		
0.0250	1.0075	0.925	309.23	0.0484
0.0450	1.0078	0.952	307.88	0.1731
0.0550	1.0079	0.958	307.05	0.1880
0.0650	1.0081	0.971	306.07	0.2270
0.0750	1.0083	0.984	305.49	0.2610
0.0850	1.0086	1.003	304.32	0.3170
		T=308.15 K		
0.0249	1.0044	0.742	311.40	0.0340
0.0449	1.0047	0.765	309.56	0.1729
0.0548	1.0049	0.776	308.69	0.2169
0.0648	1.0051	0.787	307.49	0.2630
0.0748	1.0053	0.795	306.25	0.2800
0.0847	1.0055	0.809	305.47	0.3280
		T=318.15 K		
0.0248	1.0005	0.622	313.83	-0.0114

Table 2: (Continued)

Apparent molar volume, Viscosity *B*-coefficient .... 318.15 K

c/(mol· dm^{-3})	ρ / (g· cm^{-3})	η/ (mPa·s)	V_ϕ /(cm^3·mol^{-1})	(η_r - 1) / $\sqrt{C}$
0.0447	1.0007	0.633	311.53	0.0820
0.0546	1.0009	0.642	310.34	0.1300
0.0646	1.0011	0.653	309.43	0.1900
0.0745	1.0013	0.661	308.17	0.2230
0.0844	1.0016	0.673	306.85	0.2800

[a] Molarity of ascorbic acid in water in mol·dm^{-3}

Table 3. Partial molar volume V_ϕ^0, and adjustable parameters A_v and B_v for TBAB in different aqueous ascorbic acid solutions with standard deviations σ at different temperatures.

T/K	V_ϕ^0 ($cm^3 \cdot mol^{-1}$)	A_V/($cm^3 \cdot mol^{-1.5}$)	B_V/($cm^3 \cdot mol^{-2}$)	σ
		0.00[a]		
298.15	292.78	57.61	-209.64	1.80
308.15	295.25	51.86	-200.49	1.86
318.15	299.31	40.25	-174.77	1.84
		0.05[a]		
298.15	294.35	77.76	-269.33	2.14
308.15	299.03	54.81	-221.17	2.17
318.15	306.46	36.30	-166.28	1.89
		0.10[a]		
298.15	305.86	25.09	-149.54	0.06
308.15	308.83	12.65	-132.15	0.08
318.15	312.14	5.23	-106.42	0.10
		0.15[a]		
298.15	308.69	25.05	-136.55	0.07
308.15	311.98	19.15	144.14	0.06
318.15	315.94	7.13	-131.29	0.06

[a] Molarity of ascorbic acid in water in $mol \cdot dm^{-3}$

Table 4. Values of various coefficients of Eq. 4 for TBAB in different aqueous ascorbic acid solutions

Aqueous ascorbic acid solution/($mol \cdot dm^{-3}$)	a_0/($cm^3 \cdot mol^{-1}$)	a_1/($cm^3 \cdot mol^{-1} \cdot K^{-1}$)	a_2/($cm^3 \cdot mol^{-1} \cdot K^{-2}$)
0	949.54	-4.5731	0.008
0.05	1418.1	-7.8686	0.0137
0.1	373.5	-0.7337	0.0017
0.15	518.38	-1.7021	0.0034

Table 5. Partial molar expansibility ϕ_E^0 for TBAB in different aqueous ascorbic acid solutions at different temperatures

Aqueous Ascorbic Acid solutions/(mol· dm^{-3})	ϕ_E^0 /(cm^3·mol^{-1}·K^{-1})			$\left(\partial\phi_E^0/\partial T\right)_P$ /(cm^3·mol^{-1}·K^{-2})
	298.15K	308.15K	318.15K	
0	0.197	0.357	0.517	0.016
0.05	0.301	0.575	0.849	0.024
0.1	0.280	0.314	0.348	0.003
0.15	0.325	0.393	0.461	0.007

Table 6. Values of *A* and *B* coefficients with standard errors for TBAB in different aqueous ascorbic acid solutions at different temperatures.

Aqueous Ascorbic Acid solution /(mol. dm^{-3})	$A/(cm^{3/2}\cdot mol^{-1/2})$			$B/(cm^{3}\cdot mol^{-1})$		
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
0	0.013 (±0.008)	0.011 (±0.005)	-0.029 (±0.009)	0.368 (±0.030)	0.493 (±0.020)	0.563 (±0.040)
0.05	-0.007 (±0.006)	-0.076 (±0.011)	-0.116 (±0.0140)	0.809 (±0.030)	0.926 (±0.040)	0.945 (±0.060)
0.1	-0.010 (±0.014)	-0.024 (±0.019)	-0.011 (±0.026)	1.338 (±0.06)	1.430 (±0.08)	1.597 (±0.109)
0.15	-0.247 (±0.030)	-0.283 (±0.025)	-0.367 (±0.030)	1.892 (±0.130)	2.102 (±0.102)	2.179 (±0.120)

Table 7. Partial molar volumes V_ϕ^0, Partial molar volumes of transfer, ΔV_ϕ^0, viscosity *B* coefficients, and Viscosity *B*-coefficients of transfer, Δ*B*, from water to different aqueous ascorbic acid solutions for TBAB at three different temperatures.

Aqueous Ascorbic Acid solutions /(mol· dm^{-3})	V_ϕ^0 /(cm^3· mol^{-1})	ΔV_ϕ^0 /(cm^3· mol^{-1})	B/(cm^3· mol^{-1})	ΔB/(cm^3· mol^{-1})
		T= 298.15 K		
0	292.78	0	0.368	0
0.05	294.35	1.57	0.809	0.441
0.1	305.86	13.08	1.338	0.970
0.15	308.69	15.91	1.892	1.524
		T= 308.15 K		
0	295.25	0	0.493	0
0.05	299.03	3.78	0.926	0.433
0.1	308.83	13.58	1.430	0.937
0.15	311.98	16.73	2.102	1.609
		T= 318.15 K		
0	299.31	0	0.563	0
0.05	306.46	7.15	0.945	0.382
0.1	312.14	12.83	1.597	1.034
0.15	315.94	16.63	2.179	1.616

Table 8. Values of $\bar{V}_2^{0} - \bar{V}_1^{0}$, $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$, $T\Delta S^{o}{}_2^{\neq}$, and $\Delta H^{o}{}_2^{\neq}$ for TBAB in different aqueous ascorbic acid solutions at different temperatures

Parameters	298.15 K	308.15 K	318.15 K
0.00 mol·dm^{-3}			
$(\bar{V}_2^{0} - \bar{V}_1^{0})\cdot 10^6/(\text{m}^3\cdot \text{mol}^{-1})$	274.71	277.13	281.12
$\Delta\mu_1^{0\neq}/(\text{kJ}\cdot \text{mol}^{-1})$	9.17	8.65	8.20
$\Delta\mu_2^{0\neq}/(\text{kJ}\cdot \text{mol}^{-1})$	50.73	70.00	82.17
$T\Delta S^{o}{}_2^{\neq}/(\text{kJ}\cdot \text{mol}^{-1})$	-468.75	-484.47	-500.20
$\Delta H^{o}{}_2^{\neq}/(\text{kJ}\cdot \text{mol}^{-1})$	-418.02	-414.47	-418.02
0.05 mol·dm^{-3}			
$(\bar{V}_2^{0} - \bar{V}_1^{0})\cdot 10^6/(\text{m}^3\cdot \text{mol}^{-1})$	276.07	280.69	288.05
$\Delta\mu_1^{0\neq}/(\text{kJ}\cdot \text{mol}^{-1})$	9.21	8.71	8.21
$\Delta\mu_2^{0\neq}/(\text{kJ}\cdot \text{mol}^{-1})$	110.05	129.73	136.01
$T\Delta S^{o}{}_2^{\neq}/(\text{kJ}\cdot \text{mol}^{-1})$	-387.00	-399.98	-412.96
$\Delta H^{o}{}_2^{\neq}/(\text{kJ}\cdot \text{mol}^{-1})$	-276.95	-270.25	-276.95
0.10 mol·dm^{-3}			
$(\bar{V}_2^{0} - \bar{V}_1^{0})\cdot 10^6/(\text{m}^3\cdot \text{mol}^{-1})$	287.37	290.27	293.51
$\Delta\mu_1^{0\neq}/(\text{kJ}\cdot \text{mol}^{-1})$	9.19	8.68	8.29
$\Delta\mu_2^{0\neq}/(\text{kJ}\cdot \text{mol}^{-1})$	179.67	197.73	227.09
$T\Delta S^{o}{}_2^{\neq}/(\text{kJ}\cdot \text{mol}^{-1})$	-706.97	-730.69	-754.40
$\Delta H^{o}{}_2^{\neq}/(\text{kJ}\cdot \text{mol}^{-1})$	-527.31	-532.95	-527.31
0.15 mol·dm^{-3}			
$(V_2^{0}-V_1^{0})\cdot 10^6/(\text{m}^3\cdot \text{mol}^{-1})$	289.99	293.22	297.10
$\Delta\mu_1^{0\neq}/(\text{kJ}\cdot \text{mol}^{-1})$	9.32	8.79	8.38
$\Delta\mu_2^{0\neq}/(\text{kJ}\cdot \text{mol}^{-1})$	251.08	287.39	306.33
$T\Delta S^{o}{}_2^{\neq}/(\text{kJ}\cdot \text{mol}^{-1})$	-823.61	-851.23	-878.86
$\Delta H^{o}{}_2^{\neq}/(\text{kJ}\cdot \text{mol}^{-1})$	-572.53	-563.84	-572.53

Table 9. Molality(*m*), density(*ρ*), sound speed(*u*), adiabatic compressibility(*β*), partial molal adiabatic compressibility(K_ϕ), limiting partial molal adiabatic compressibility(K_ϕ^0), and experimental slope(S_k^*) of TBAB in aqueous ascorbic acid solution at 298.15K

m /(mol· Kg^{-1})	*u* /(m·s^{-1})	$\beta\times10^{10}$ /(Pa^{-1})	$K_\phi\times10^{10}$ /(m^3· mol^{-1}· Pa^{-1})	$K_\phi^0\times10^{10}$ /(m^3· mol^{-1}· Pa^{-1})	$S_k^*\times10^{10}$ /(m$^{9/2}$· mol$^{-3/2}$· Pa^{-1})
0.00 mol·dm^{-3}					
0.0253	1451.9	4.7549	-2.406	-1.235 (±0.216)	-6.829 (±0.883)
0.0458	1459.6	4.7018	-2.551		
0.0561	1466.0	4.6593	-2.865		
0.0665	1471.1	4.6258	-2.947		
0.0770	1478.7	4.5764	-3.210		
0.0875	1484.5	4.5389	-3.273		
0.05 mol·dm^{-3}					
0.0253	1460.3	4.6839	-1.402	0.0201 (±0.131)	-9.238 (±0.538)
0.0458	1468.7	4.6281	-2.041		
0.0561	1473.1	4.5992	-2.202		
0.0665	1477.6	4.5701	-2.317		
0.0770	1483.4	4.5326	-2.507		
0.0875	1490.3	4.4890	-2.724		
0.10 mol·dm^{-3}					
0.0253	1467.4	4.6228	0.039	1.469 (±0.168)	-9.466 (±0.687)
0.0458	1471.9	4.5932	-0.658		
0.0561	1474.3	4.5772	-0.837		
0.0665	1476.4	4.5628	-0.939		
0.0770	1480.2	4.5385	-1.141		
0.0875	1484.0	4.5141	-1.294		
0.15 mol·dm^{-3}					
0.0253	1477.0	4.5501	0.086	1.775 (±0.0715)	-10.584 (±0.293)
0.0458	1480.5	4.5274	-0.472		
0.0561	1483.3	4.5095	-0.714		
0.0665	1487.2	4.4851	-0.980		
0.0770	1491.5	4.4584	-1.201		
0.0875	1495.0	4.4362	-1.320		

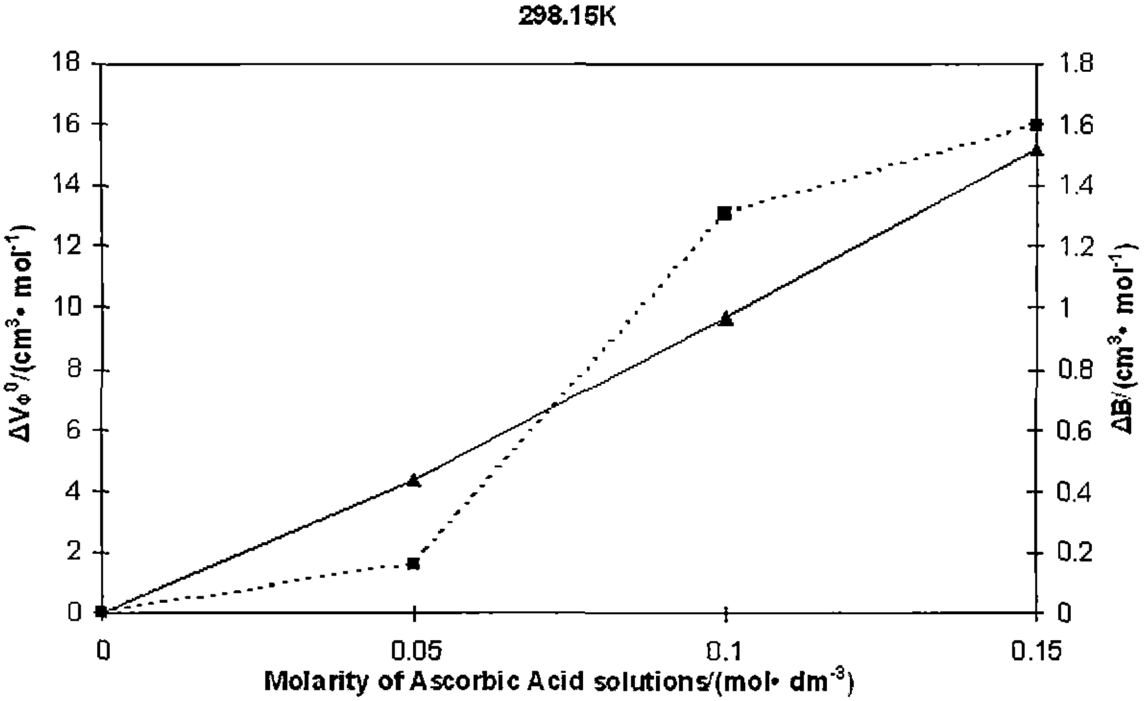

Fig. 1(a) Plots of partial molar volume (ΔV_{ϕ}^{0}) and viscosity *B*-coefficients (ΔB) against molarity for the transfer from water to different aqueous ascorbic acid solutions for TBAB at $T =$ 298.15 K. Dotted lines for ΔV_{ϕ}^{0} and solid lines for ΔB.

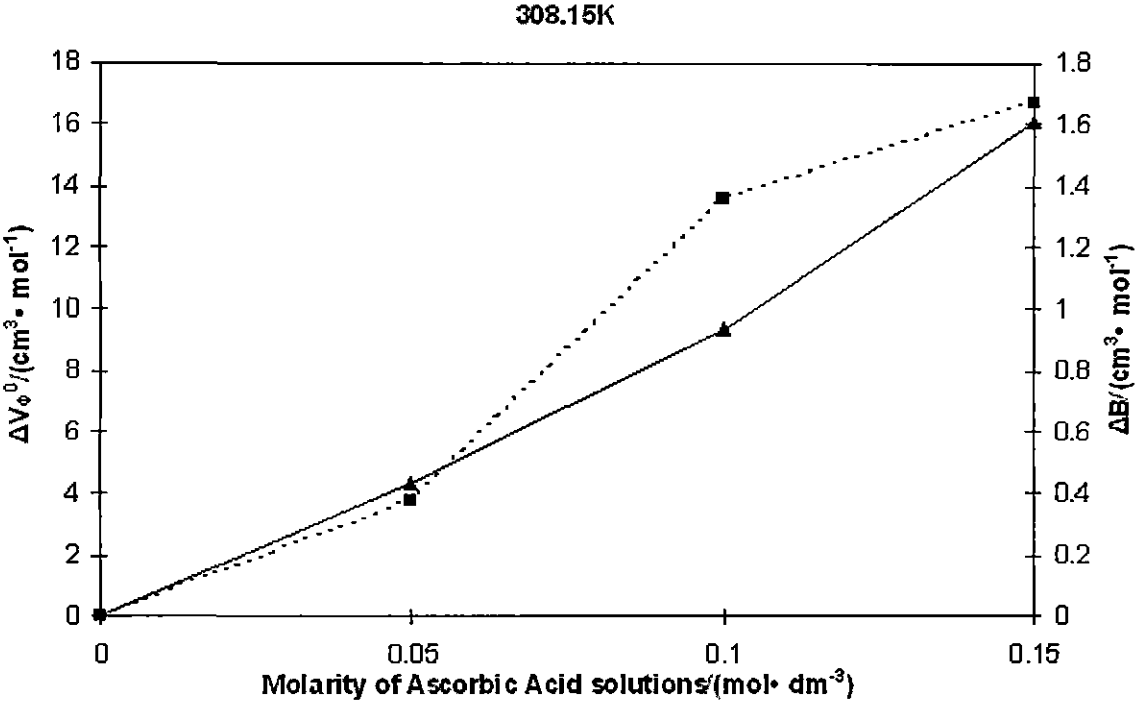

Fig. 1(b) Plots of partial molar volume (ΔV_{ϕ}^{0}) and viscosity *B*-coefficients (ΔB) against molarity for the transfer from water to different aqueous ascorbic acid solutions for TBAB at $T = 308.15$ K. Dotted lines for ΔV_{ϕ}^{0} and solid lines for ΔB.

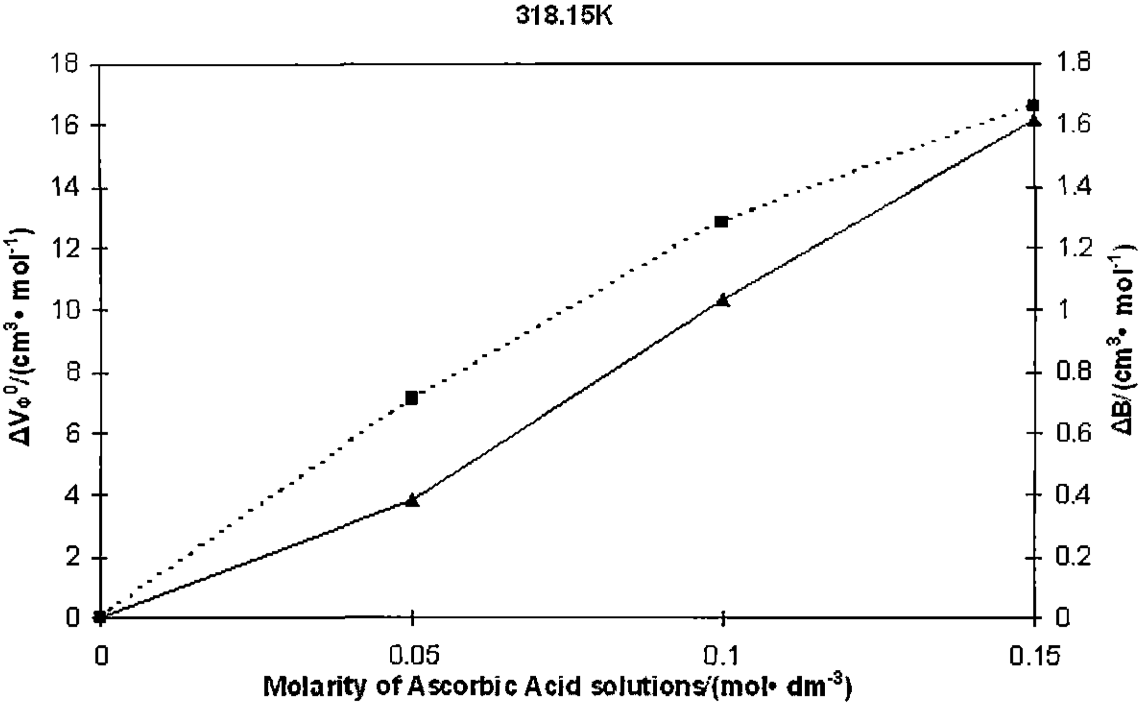

Fig. 1(c) Plots of partial molar volume (ΔV_ϕ^0) and viscosity *B*-coefficients (ΔB) against molari for the transfer from water to different aqueous ascorbic acid solutions for TBAB at $T = 318.15$ K. Dotted lines for ΔV_ϕ^0 and solid lines for ΔB.