PHYSICO-CHEMICAL AND ACOUSTICAL BEHAVIOR OF LACTOSE IN AQUEOUS SOLUTIONS OF TETRAALKYLAMMONIUM BROMIDE SALTS AT DIFFERENT TEMPERATURES

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ABSTRACT

In the present communication, experimental values of density(ρ), viscosity(η) and speed of sound (U) of lactose in aqueous solution of tetraethylammonium bromide (TEABr), tetrapropylammonium bromide(TPABr) and tetrabutylammonium bromide(TBABr) salts (0.0M, 0.05M and 0.1M) at different temperatures (303.15, 308.15 and 313.15K) are reported . These data have been used to calculate the acoustical parameters like apparent molal compressibility (Φ_k), apparent molal volume (Φ_v), the limiting apparent molal compressibility (Φ_k^o), limiting apparent molal volume (Φ_v^o) along with their constant (S_k and S_v), transfer compressibility ($\Delta\Phi_k^o$), transfer volume ($\Delta\Phi_v^o$), Falkenhagen coefficient A and viscosity B coefficient have been calculated. From the results obtained, a discussion was carried out in terms of interactions and structure factor (in the framework of ''structure-making'' or 'structure-breaking'' solutes) in these mixtures. The positive values of the viscosity B coefficient indicate structure making tendency in these systems.

Key words*:* Jone-Dole co-efficient, molecular interaction, quaternary ammonium bromide salts, saccharide, solute-solvent interaction, transfer volume.

INTRODUCTION

Ultrasonic velocity measurement is one of the best tools to understand the nature of molecular interactions and investigate the physicochemical behavior occurring in the solution. Further, these measurements are useful in various fields such as chemical, food processing, emulsification, medicine, engineering, in nuclear power plant, water treatment, dehydration of vegetables etc. In chemical industries, ultrasonic energy is used to study chemical processes and to synthesize various chemical compounds [1]. Electrolytes play significant role in chemical laboratories, industries and biological processes of living organisms [2]. An electrolytes when dissolved in water, changes the arrangement of water molecules with a strong electric field of its ions. This property of electrolytes is known as structure maker or structure breaker has been widely used to understand the effect of electrolytes on the structure and function of biomolecules in the biochemical process of the body system. Moreover, the studies of the interactions between electrolytes with saccharides are very important for some physiological process.

Saccharides and their derivatives as the most abundant class of biomolecules are known to exist in wide range of forms, which is a reflection of their biological versatility and the great diversity of their biological functions such as structural, protective, metabolic and recognition. The saccharide components of cell membranes are the receptors of biologically active compounds (enzymes, drugs, etc.) [3].Due to recognition of saccharides in various biological processes like protein/enzyme stability, protective efficacy, cellular interactions, etc., the knowledge about hydration characteristics of these compounds in aqueous solutions is very important [4]. Carbohydrate located at cell surfaces are important as receptors for the bioactive structures of hormones, enzymes, viruses, antibodies etc.[5].Interactions of electrolytes with saccharides are very important in exploring the stability of polysaccharides in biological systems as well as in the chemical industry of saccharides. It is an essential component for maintaining cell viability, a natural cell-protecting agent as well as an energy reservoir in many organisms [6].

In the present paper, we report the densities (ρ), ultrasonic speed (u) and a viscosity solution of Lactose in aqueous quaternary ammonium salts solutions (0.0M 0.05M and 0.1M) at different temperatures. Various physico-chemical parameters viz., apparent molal compressibility (Φ_k), apparent molal volume (Φ_v), the limiting apparent molal compressibility (Φ_k^o), limiting apparent molal volume (Φ_v^o) along with their constant values (S_k and S_v), the values of transfer compressibility ($\Delta\Phi_k^o$), transfer volume ($\Delta\Phi_v^o$), and coefficients A and B have been calculated using the experimental data. Consequently, in view of the above, an effort is made to delineate the solute-solute and a solute-solvent interaction in the quaternary ammonium bromide salts from volumetric properties.

MATERIALS AND METHOD

Lactose and the quaternary ammonium bromide salts of high purity used in the present studies were purchased from S.D.Fines chemicals and E-Merk (India). These chemicals were used as such without further purification. The density and ultrasonic velocity at different molality of lactose in quaternary ammonium bromide salts were measured at 303.15, 308.15, 313.15 K. The weight of the sample was measured using an electronic digital balance with a precision of ±0.0001 g (Model: - SHIMADZU AX200). An ultrasonic interferometer having the frequency 3MHz (MITTAL ENTERPRISES, NEW DELHI, MODEL F–81) with an overall accuracy of ± 2ms^{-1} has been used for velocity measurement. The density was determined using a specific gravity bottle by relative measurement method with a reproducibility of ± 0.01 kgm^{-3}.An Ostwald's viscometer (10 ml) was used for the viscosity measurement. Efflux time was determined using a digital chronometer within ± 0.01s. An electronic digital constant temperature bath (RAAGA Industries) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature.

THEROY

Apparent molal compressibility ϕ_k and apparent molal volume ϕ_v of the electrolytes were calculated by using the relations [7]:

$$\phi_k = \frac{1000}{m\rho_0}(\rho_0\beta - \beta_0\rho) + \frac{\beta_0 M}{\rho_0} \quad \text{... (1)}$$

$$\phi_v = \frac{1000}{m\rho_0}(\rho_0 - \rho) + \frac{M}{\rho_0} \quad \text{... (2)}$$

Where m is the molal concentration of the solute (lactose) ρ and ρ_0 are the densities of the solution and the solvent (aqueous quaternary ammonium salts) respectively. M is the molar mass of the solute β and β_0 the adiabatic compressibility of the solution and the solvent respectively. The values of apparent molal volume $\phi_v°$ [8][9] and apparent molal compressibility ϕ_k^0 were obtained using relations [10]:

$$\phi_k = \phi_k^0 + S_k m^{1/2} \quad \text{... (3)}$$

$$\phi_v = \phi_v° + S_v m^{1/2} \quad \text{... (4)}$$

Where the intercepts $\phi_v°$ or $\phi_k°$ by definition are free from solute-solute interaction and therefore provide a measure of solute-solvent interactions, whereas the experimental slop, S_v or S_k provide information regarding solute-solute interactions. Transfer compressibility ($\Delta\varphi_K^0$) and Transfer volume ($\Delta\varphi_v^0$) of lactose from water to aqueous quaternary ammonium solutions at infinite dilutions have been estimated as below:

$$\Delta\varphi_K^0 = \varphi_{K(aq.\text{quaternary ammonium salts})}^0 - \varphi_K^0\,(\text{in water}) \quad \text{...(5)}$$

$$\Delta\phi_v° = \phi_v°_{(aq.\text{quaternary ammonium salts})} - \phi_v°\,(\text{in water}) \quad \text{...(6)}$$

. The viscosity data have been analyzed by using the Jones-Dole equation [11]

$$\frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm \quad \text{....(7)}$$

where η and η_0 are the viscosities of the solute and solvent respectively, A is a known as Falkenhagen coefficient and B is Jones-Dole coefficient [11]. Coefficient A accounts for the solute-solute interactions and B is a measure of structural modifications induced by the solute-solvent interactions. -

RESULTS AND DISCUSSIONS

The following observations have been made on apparant molal compressibility (Φ_k) and apparent molal volume Φ_v (Fig.1) for lactose in purely aqueous solutions as well as in the presence of the quaternary ammonium bromide salts at different temperatures.

i. The values of (Φ_k) are all negative over the entire range of molality of lactose and increase (negatively decrease) with increase in concentration of electrolyte content as well as with rise in temperatures

ii. A linear relation between Φ_k and solute concentration has been observed throughout the entire range.

iii. In all the three system, the maximum negative values of Φ_k are recorded in 0.0M electrolyte content in the system.

It can be observed that Φ_k varies linearly with molality of the solution for all the temperatures studied and become less negative with rise in temperature. It may be due to the fact that at lower temperature, water around the solute molecule is tightly bound to the solute and it yields a high negative value of Φ_k[12] .The limiting apparent molal compressibility (Φ_k^0) and experimental slopes (S_k) provide information regarding the solute-solvent and solute-solute interactions in the mixture respectively. The observed negative values of Φ_k^0 (Table 1) in all the systems indicates that the water molecules around the solutes are less compressible than water molecules in the bulk solution, which is attributed to strong attractive interactions in these systems. The values of S_K are positive in all the systems. Appreciable negative values of Φ_k^0 for the above system strongly confirm the existence of solute-solvent interactions. The positive values of S_k indicate the presence of ion-ion or solute-solute interaction in the system [13].

The following observations have been made on apparent molal volume Φ_v (Fig.2) of the saccharide in aqueous solutions of electrolyte at different temperatures.

i. The values of Φ_v are all negative over the entire range of molality of lactose and seem to be increasing with increase in concentration of salt content as well as with rise in temperatures.

ii. A linear relation between Φ_v and solute concentration has been observed throughout the entire range.

iii. In all the ternary systems, the maximum negative values of Φ_v are obtained in 0.0M salts content.

The negative values of apparent molal volume (Φ_v) indicate the greater presence of solute-solvent interaction and electrostrictive solvation of ions [13] .The limiting apparent molal volume behavior of a solute at infinite dilution is satisfactorily represented by Φ_v° which is independent of solute-solute interactions and provides information concerning solute-solvent interactions. Table 3.11 reveals that Φ_v° is negative for all the solutions [14] which suggest the electrostrictive solvation of the ions [15]. The magnitude of S_v is an interactional parameter positive for all concentrations of electrolytic solutions at different temperatures indicates toward the presence of ion-ion interactions [16].

The thermodynamic transfer functions can be explained in terms of structure-making and structure-breaking effects of the solute as has been postulated by Frank and Evans [17].The limiting apparent molar properties of transfer provide qualitative as well as quantitative information regarding solute-solvent interactions without taking into account the effects of solute-solute interactions [14]. From the Table 2, it is observed that the transfer compressibility ($\Delta\phi_k^0$) values are positive and clearly decrease with increase in concentration of quaternary ammonium salts as observed by Amalendu Pal [18]. The observed positive transfer compressibility ($\Delta\phi_k^0$) suggests that the hydrophilic-ionic groups and hydrophilic-hydrophilic group interactions are dominating in these systems [19].

From the Table 2, it is observed that the values of transfer volume ($\Delta\phi_v^0$) are both positive and negative in all the systems at different temperatures. The sign of $\Delta\phi_v^0$ is often interpreted in terms of

strength of solute-co-solute interactions as explained on the basis of co-sphere overlap model developed by Gurney (1953)[20] and Frank and Evans 1945 [17] .When the $\Delta\phi_v^0$ values are positive, the hydrophilic-hydrophilic group interactions are considered to be predominant, while the hydrophilic-hydrophobic group interactions are thought to contribute negatively to the $\Delta\phi_v^0$ [14].

The viscosity is another important parameter to understand the structure and molecular interaction occurring in the solution and its variation is attributed to the structural changes. The viscosity coefficient A represents the ion-ion interactions coupled with the size and shape effect of the solute and to some extent, solute-solvent interactions [21]. On close scrutiny of the resultant values of both A and B co-efficient, it has been found that the values of A are both negative and positive for all the systems while the B-coefficient are only positive at different temperatures (Table 3). Since the A coefficient reflecting ionic interactions, the negative values of A coefficient point towards weak ion-ion interactions [22] while the positive values of A indicate the strong solute-solute interactions [23]

The viscosity B coefficient is a valuable tool to provide information concerning the solvation of the solutes and their effects on the structure of the solvent. Further, the effects of solute-solvent interactions on the solution viscosity can be inferred from the B-coefficient. [24]. The positive Jone Dole B coefficient indicates the presence of strong solute-solvent interactions [22] whereas negative values of *B* co-efficient indicate presence of solute-solvent interactions. From the Table 3, it is observed that the values of *B*-coefficient are all positive thereby suggesting the presence of strong solute-solvent interactions in the systems [24].Further the positive values of viscosity B co-efficient indicates the kosmotropes i.e. structure-making capacity of the solute in the systems [25].

CONCLUSIONS

In this study, experimental results for density, ultrasonic velocity and viscosity data have been observed for lactose in aqueous solutions of quaternary ammonium bromide salts at different temperatures. The derived acoustical parameters such as ϕ_k, ϕ_v, ϕ_k^0, ϕ_v^0, viscosity B coefficient etc., have been used to analyse the molecular interactions in the solutions. The existence of ion-solvent interactions results in the structure making property while solute-solute interactions are responsible for structure-breaking properties of electrolytes in these systems. From the magnitude of B coefficient, it can be concluded that the structure making tendency of lactose is observed in the aqueous medium and the strength of interactions is in the order TEABr>TBABr>TPABr. Hence, Tetraethylammoniumbromide (TEABr) behaves as a good structure maker. Further, the observed positive values of transfer adiabatic compressibility ($\Delta\phi_k^0$) suggest that the hydrophilic-ionic groups and hydrophilic-hydrophilic group interaction are dominating in these systems.

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Table 1

Values of Limiting apparent molal compressibility (Φ_k^0), slope (S_k) and Transfer compressibility ($\Delta\Phi_k^0$) of lactose in aqueous solution of Tetraethylammonium bromide (TEABr), Tetrapropylammonium bromide (TPABr), and Tetrabutylammonium bromide(TBABr) at 303.15, 308.15 and 313.15K

Tetra alkyl ammonium bromide salts	Molality (M)	Limiting apparent molal compressibility $\Phi_k^0/(10^{-7}\ m^2\ N^{-1})$			Constant $S_k/(10^{-7}\ N^{-1}\ m^{-1}.mol^{-1})$			Transfer compressibility $\Delta\Phi_k^0/(10^{-7}\ m^2\ N^{-1})$		
		Temperature (K)								
		303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
Aqueous TEABr	0.00	-5.14	-5.00	-3.45	9.09	10.38	5.19	-	-	-
	0.05	-3.18	-2.98	-2.32	4.00	4.06	2.51	1.96	2.04	1.13
	0.1	-3.63	-2.91	-2.57	5.59	3.49	2.53	1.51	2.09	0.88
Aqueous TPABr	0.00	-5.14	-5.00	-3.45	9.09	10.38	5.19	-	-	-
	0.05	-3.20	-3.13	-2.97	3.82	3.93	3.92	1.94	1.89	0.48
	0.1	-3.85	-3.65	-2.91	6.14	5.58	3.16	1.29	1.35	0.54
Aqueous TBABr	0.00	-5.14	-5.00	-3.45	9.09	10.38	5.19	-	-	-
	0.05	-3.29	-3.10	-3.14	3.40	2.86	3.96	1.85	1.8	0.31
	0.1	-3.99	-3.63	-3.24	5.49	4.85	4.05	1.15	1.37	0.21

Table 2

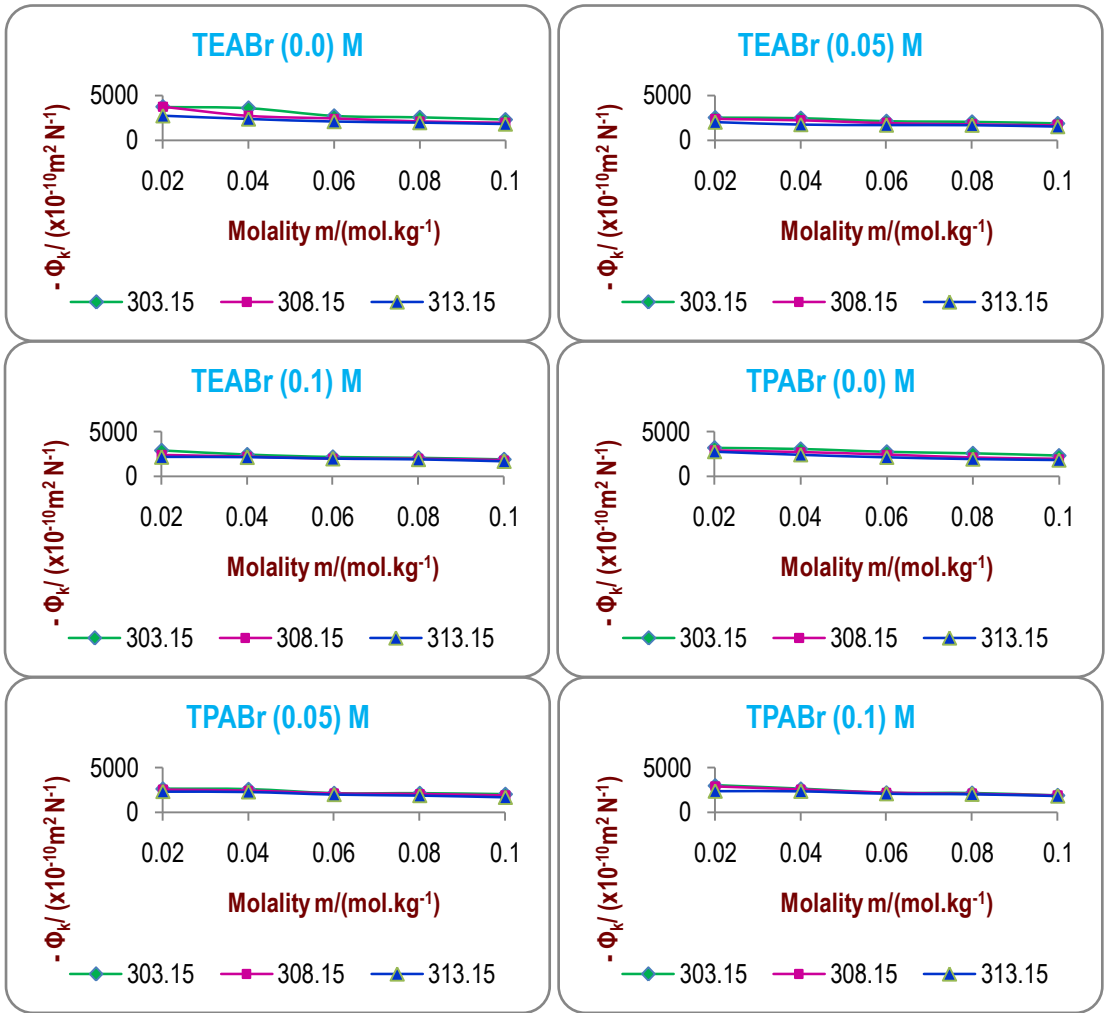
Values of Limiting apparent molal volume (Φ_v^0), slope (S_v) and Transfer volume ($\Delta\Phi v^0$) of lactose in aqueous solution of Tetraethylammonium bromide (TEABr), Tetrapropylammonium bromide (TPABr), and Tetrabutylammonium bromide(TBABr) at 303.15, 308.15 and 313.15K

Tetra alkyl ammonium bromide salts	Molality (M)	Limiting apparent molal volume (Φ_v^0) /(m^3. mol^{-1})			Constant S_v /(m^3 $kg^{1/2.}$ $mol^{-3/2}$)			Transfer volume $\Delta\Phi_v^0$/(m^3. mol^{-1})		
		Temperature (K)								
		303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
Aqueous TEABr	0.00	-210.29	-248.70	-170.68	402.74	564.40	245.91	-	-	-
	0.05	-159.05	-128.70	-128.38	230.64	134.06	152.03	51.24	120.00	42.30
	0.1	-213.16	-219.74	-218.05	234.07	269.50	335.82	-2.87	28.96	-47.37
Aqueous TPABr	0.00	-210.29	-248.70	-170.68	402.74	564.40	245.91	-	-	-
	0.05	-218.16	-220.92	-206.23	245.96	283.68	273.48	-7.87	27.78	-35.25
	0.1	-333.46	-219.85	-212.11	638.25	224.51	275.81	-123.17	28.85	-41.43
Aqueous TBABr	0.00	-210.29	-248.70	-170.68	402.74	564.40	245.91	-	-	-
	0.05	-362.86	-269.38	-290.45	699.79	240.15	427.13	-152.57	-20.68	-119.47
	0.1	-296.17	-386.64	-391.19	516.73	828.64	856.45	-85.88	-138.61	-220.51

Table 3

Values of Falkenhagen coefficients (A) and Jones-Dole coefficients (B) of lactose in aqueous solution of Tetraethylammonium bromide (TEABr), Tetrapropylammonium bromide (TPABr), and Tetrabutylammonium bromide (TBABr) at 303.15, 308.15 and 313.15K

Tetra alkyl ammonium bromide salts	Molality (M)	$A/(dm^{3/2}.mol^{-1/2})$			$B/(dm^{3}.mol^{-1})$		
		Temperature (K)					
		303.15	308.15	313.15	303.15	308.15	313.15
Aqueous TEABr	0.00	0.1530	-0.0059	-0.1994	0.9366	2.0127	1.8584
	0.05	0.0160	0.2865	-0.0409	1.2259	0.7981	1.9136
	0.1	-0.0521	0.0175	-0.1106	0.9983	1.8999	1.9518
Aqueous TPABr	0.00	0.1530	-0.0059	-0.1994	0.9366	2.0127	1.8584
	0.05	0.2782	0.4264	0.0568	0.2760	0.1779	1.3874
	0.1	0.0802	0.0983	0.2383	0.9483	1.2594	0.5383
Aqueous TBABr	0.00	0.1530	-0.0059	-0.1994	0.9366	2.0127	1.8584
	0.05	0.0920	0.0422	0.1494	0.6130	0.7040	0.8905
	0.1	0.0842	0.0668	0.1734	0.9599	0.9811	0.6267


TEABr (0.0) M
TEABr (0.05) M
TEABr (0.1) M
TPABr (0.0) M
TPABr (0.05) M
TPABr (0.1) M
5000
0
0.02
0.04
0.06
0.08
0.1
Molality m/(mol.kg-1)
- Φk/ (x10-10m2 N-1)
303.15
308.15
313.15

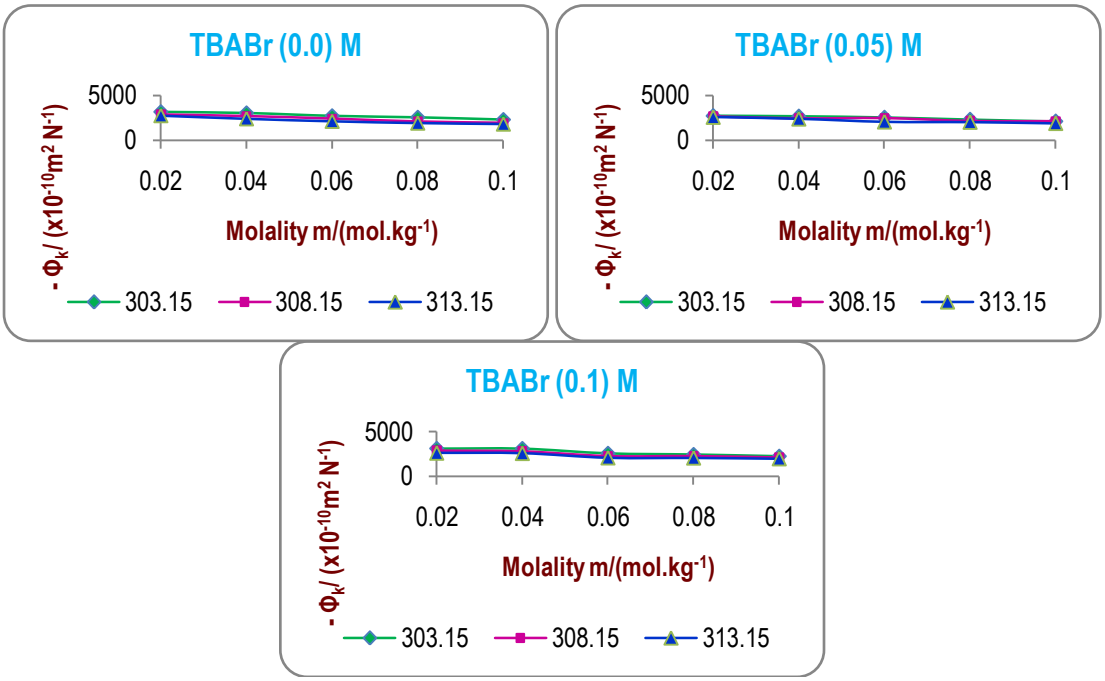
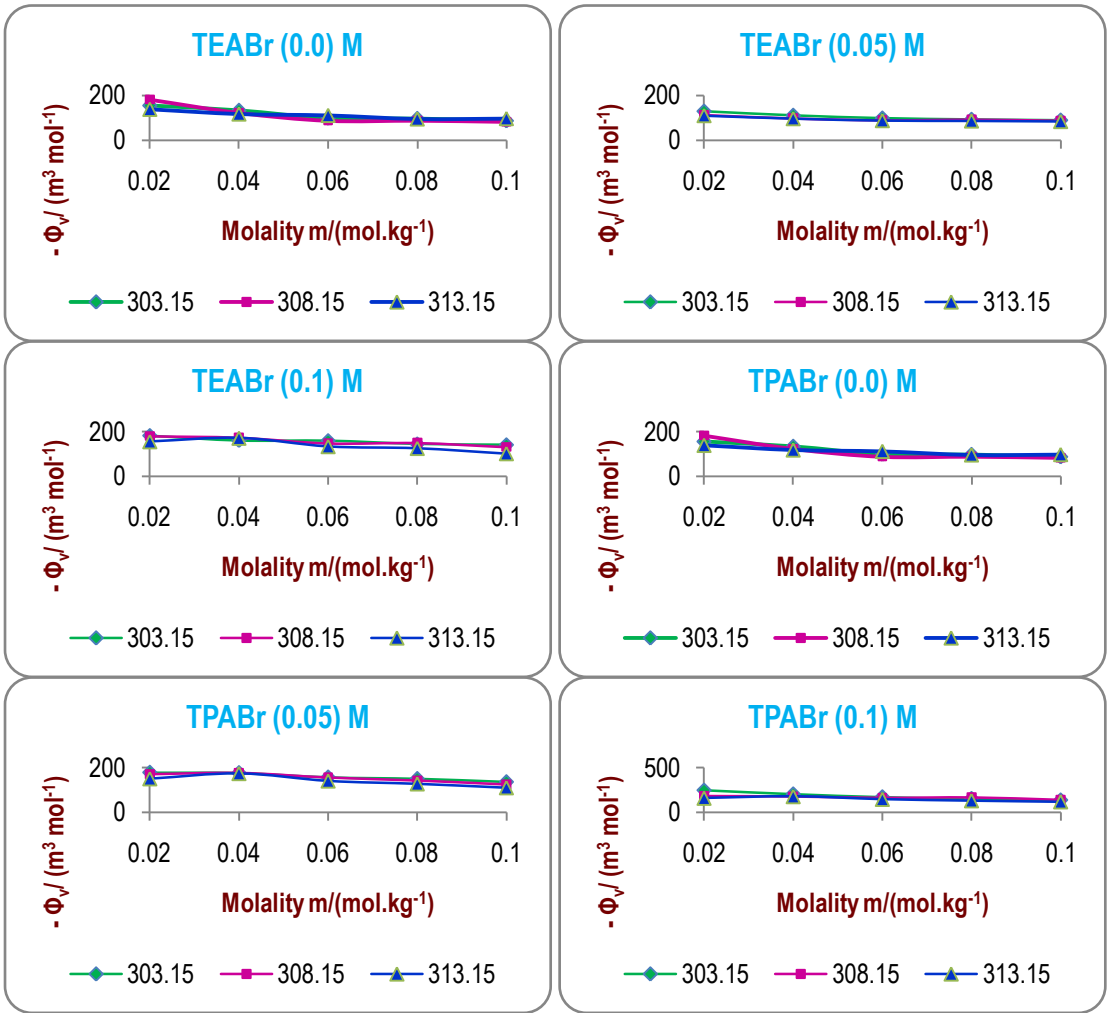


Fig. 1: Values of Apparent molal volume (Φ_k) of lactose in aqueous solution of Tetraethylammonium bromide (TEABr), Tetrapropylammonium bromide (TPABr) and Tetrabutylammonium bromide (TBABr) at 303.15, 308.15 and 313.15K


TEABr (0.0) M
TEABr (0.05) M
TEABr (0.1) M
TPABr (0.0) M
TPABr (0.05) M
TPABr (0.1) M
- Φv/ (m3 mol-1)
Molality m/(mol.kg-1)
200
0
500
0.02
0.04
0.06
0.08
0.1
303.15
308.15
313.15

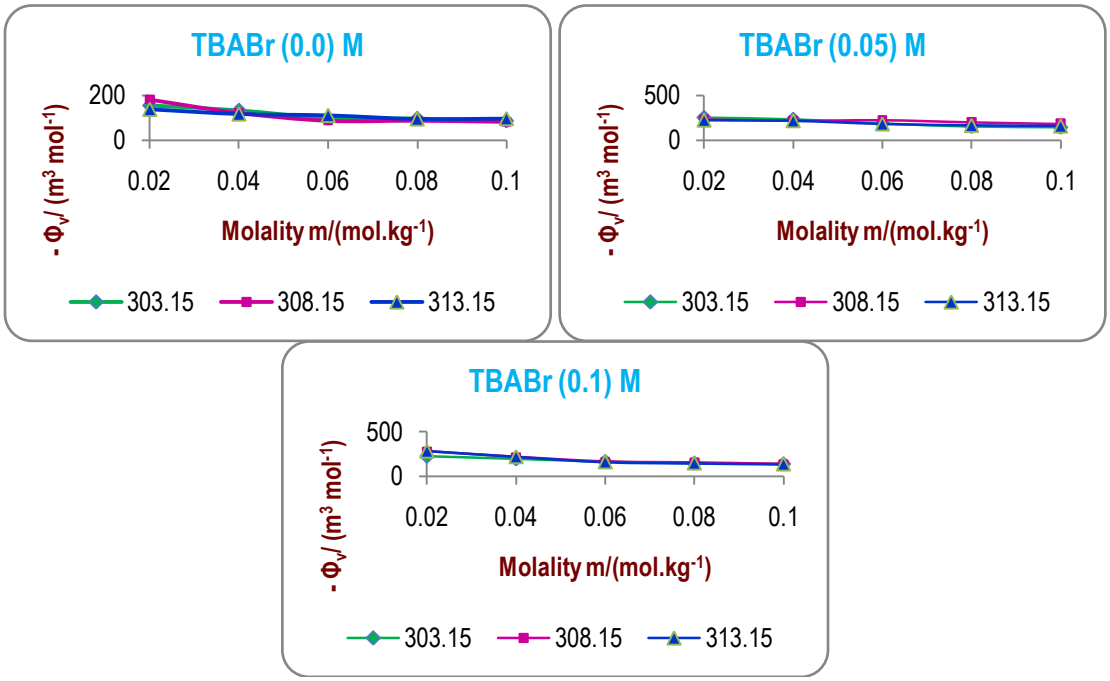


Fig. 2: Values of Apparent molal volume (Φ_v) of lactose in aqueous solution of Tetraethylammonium bromide (TEABr), Tetrapropylammonium bromide (TPABr) and Tetrabutylammonium bromide (TBABr) at 303.15, 308.15 and 313.15K