Molecular interionic interaction studies of kcl and k2so4 at 303k

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Abstract - Potassium (K) can be applied as a straight fertilizer or as part of a blended or compound fertilizer with nitrogen and phosphorous. Plants absorb potassium in its ionic form K$^+$. Potassium is associated with movement of water, nutrients, and carbohydrates in plant tissue. Potassium stimulates early growth, increases protein production, improves the efficiency of water use, improves resistance to drought, diseases and insects, aids in photosynthesis and food formation, reduces respiration, preventing energy losses, and enhances translocation of sugars and starch. The study of the properties of aqueous and binary solutions is very important in many areas of science and researches and is progressing in the direction with a view to know more about the structure of water. The ultrasonic velocity, density, and viscosity of potassic fertilizer solutions were experimentally measured at different molalities at 303K. From the measured experimental datas, hydration parameters such as molal hydration number (n_h'), apparent molal compressibility (ϕ_k), apparent molal volume (ϕ_v), molar solvated volume (ϕ_s), limiting apparent molal compressibility (ϕ_k^o), limiting apparent molal volume (ϕ_v^o), their constants (S_k and S_v) and viscosity B-coefficient were calculated for the aqueous potassium sulphate (K$_2$S0$_4$) and potassium chloride (KCl). A comparative study was done against potassium sulphate and potassium chloride solutions through these hydration parameters. It was found that molecular association is dominant in potassium sulphate than potassium chloride.

IndexTerms-Hydration number, apparent molal compressibility, apparent molal volume, molar solvated volume, viscosity B coefficient.
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I. INTRODUCTION

The ultrasonic studies provide information about the state of solute in solvent media. Ultrasonic investigation in aqueous solutions of electrolytes and non-electrolytes provides useful information in understanding the degree and nature of interaction because intramolecular and intermolecular association related to structural changes affects the ultrasonic velocity[1]. Various interactions exist between the ions in solution helps in understanding the nature of solute and solvent, whether the solute modifies or distorts the structure of the solvent. The solute added to the solvent causes a volume contraction due to interaction with the molecules of solvent and this may influence other acoustical properties of solutions.

The hydration number, apparent molal volume and apparent molal compressibility are proven to be a very useful tool in elucidating the structural interactions occurring in solutions. Consequently, study of the volumetric properties in aqueous salt solutions is very useful to obtain information about various types of interactions such as solute-solute, solute-solvent, ion-solvent and ion-ion interactions in the solutions. Owing to these considerations, the comparative study on hydration properties has been made to elucidate the inter ionic interactions of potassium sulphate (K$_2$SO$_4$) and potassium chloride (KCl) in water at 303K. To shed more light on such information the values of molal hydration number (n_h'), apparent molal compressibility *(ϕ_k),* apparent molal volume *(ϕ_v),* limiting apparent molal compressibility *(ϕ_k^0),* limiting apparent molal volume *(ϕ_v^0)* and their constants (S$_K$, S$_V$), molar solvated volume *(ϕ_s),* and viscosity A and B coefficient of Jones-Dole equation have been calculated.

II. MATERIALS AND METHODS

The present study was carried out using AR grade chemicals. Double distilled water was used for the preparation of solutions. A special thermostatic water bath arrangement was used for ultrasonic velocity, density and viscosity measurements and temperature was maintained within $\pm$0.1°C. Dual frequency interferometer (Mittal Enterprises, model F-81D) with an accuracy of 0.5% and the frequency of 2MHz was used in the present work for the measurement of ultrasonic velocity of solutions. Densities and viscosities of the solution were measured by relative method.

III. THEORY OF EVALUATED PARAMETERS

Adiabatic compressibility (β) can be determined with the measurement of density ρ and ultrasonic velocity U as

$$\beta = \frac{1}{U^2 \rho} \qquad \text{Kg}^{-1} \text{ ms}^2 \qquad\qquad \text{-----(1)}$$

Molal hydration number (n_h') is given by

$$n_h^{'} = \frac{n_1}{n_2}\left(1 - \frac{\beta}{\beta_o}\right) \qquad\qquad \text{-----(2)}$$

where β and β$_0$ are the compressibilities of solvent and solution respectively, n$_1$ and n$_2$ are the number of moles of solvent and solution respectively.

The apparent molal compressibility ϕ_k of a solute is the compressibility of an amount of solution containing one mole of the solute minus the compressibility of the solvent in water and is obtained by

$$\phi_k = \frac{1000}{n_2 \rho_0}(\rho_o \beta - \beta_o \rho) + \frac{\beta_o M_2}{\rho_o}$$
-----(3)

ϕ_k as a function of m is obtained by Gucker from Debye Huckel theory and is given by

$$\phi_k = \phi_k^o + S_k m^{1/2}$$
-----(4)

where ϕ_k^0 is the limiting apparent molal compressibility at infinite dilution and S_k is a constant. ϕ_k^0 and S_k of equation (4) have been evaluated by least square method.

The apparent molal volume ϕ_v of the solute is the volume of the amount of the solution containing one mole of the solute minus the volume of water present in the solution and is calculated by

$$\phi_v = \frac{1000}{n_2 \rho_o}(\rho_o - \rho) + \frac{M_2}{\rho_o}$$
-----(5)

The apparent molal volume has been found to differ with concentration according to Masson's empirical relation as,

$$\phi_v = \phi_v^o + S_v m^{1/2}$$
-----(6)

where ϕ_v^0 is the limiting apparent molal volume at infinite dilution and S_v is a measure of solute-solute interactions and these value were determined by least square method.

The molal solvated volume ϕ_s can be obtained by the relation

$$\phi_s = \phi_v + n_h V_1$$
-----(7)

The entire viscosity data have been analyzed in the light of Jones-Dole semi empirical equation

$$\frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm$$
-----(8)

where η and η_0 are the viscosity of the solution and solvent respectively and m is the molal concentration of the solute-solvent system. A and B are constants which are definite for a solute-solvent system. A is known as the Falkenhagen coefficient which characterizes the ionic interaction and B is the Jones-Dole or viscosity B-coefficient which depends on the size of the solute and the nature of solute-solvent interactions.

IV. RESULTS AND DISCUSSION

The adiabatic compressibility shows a decreasing trend with increase in concentration for both the systems (table 1) confirms the increasing electrostrictive compression of solvent around the solute molecules that resulted in a larger decease in the compressibility of solutions[2-4]. Similar result of decrease in adiabatic compressibility and intermolecular free length with increase in concentration was reported by Vijayta Gupta et.al in aqueous sodium chloride and potassium chloride solutions[5]. The decrease in adiabatic compressibility with increase in concentrations confirms the presence of ion-solvent interactions through ion-dipole interactions between solute ions and surrounding water molecules. Because when an ion is added to water, it attracts certain water molecules towards itself by moving with a violent twist in the bulk of the water molecules due to the force of electrostriction[6]. Because of this, the available water molecules for the next incoming ions decreased. This closeness is called the compression.

Every solvent has the limiting compressibility. The compressibility of a solvent is higher than that of solution and it decreases with the increase in concentration of the solution. With increase in ionic concentrations, their electrostrictive forces cause the structure to break and the solute surrounded water molecules are more compactly packed. This effect in turn reduces the compressibility with increased solute concentration. The degree of hydration is measured by a quantity known as hydration number assigned to each individual ion. It is observed that the values of n_h' are positive (table 1) for both the systems taken for the study and it indicates an appreciable solvation of solutes[7]. This is an added support for the structure promoting nature of the solutes as well as the presence of dipolar interaction between the solute and water molecules. This also suggests that compressibility of the solution is less than that of the solvent. As a result, solute will gain mobility and have more probability of contacting solvent molecules. This may enhance the interaction between solute and solvent molecules[8]. For potassium chloride, n_h' increases upto 0.15m and then decreases. At low molalities, ions get enough time to contact the water molecules. These situations increase the interaction between ions and water molecules. The values of hydration number are found to be continuously decreasing for potassium sulphate except at 0.35m.This decreasing trend may be due to the lack of free solvent molecules in secondary solvation shell because hydration occurring in electrolytes is assumed mainly due to free solvent molecules in secondary solvation shell. The decreasing behaviour shows the strength of interaction gets weakened between solute-solvent molecules[9]. Further this decreasing trend indicates that the addition of electrolytes introduces a dehydration effect in solution[10]. Similar results were reported by R.Palani and M.Marshal Arunkumar[11]. The regular decrease in hydration number with increase in solute content (fig.2) indicates the decrease in size of secondary layer of solution and formation of weak bond in primary layer[12].From the magnitude of n_h', it can be concluded that stronger molecular association is found in potassium sulphate than potassium chloride. The variations of ϕ_k with concentration for both systems are represented graphically in figure (3). The ϕ_k values are all negative (table 1) for the entire range of molality. It is well known that solutes causing electrostriction lead to

decrease in the compressibility of the solution. This is reflected by the negative values of ϕ_k of the systems. The negative values of apparent molal compressibility indicate the hydrophilic interactions occurring in these systems. Since, more number of water molecules is available at lower concentration of solution, the chances for the penetration of solute molecules into the solvent molecules are highly favoured. This is indicated by the maximum values of ϕ_k at lower concentration for the systems[13]. The negative values of ϕ_k indicating the ionic interaction occurring in these solutions, which also indicate the strengthening of ion-solvent interaction in these solutions. The limiting apparent molal compressibility ϕ_k^0 provides information regarding ion-solvent interaction and its associated constant S_k that of ion-ion interaction in the solutions. It is observed that ϕ_k^0 values are negative for both the systems (table 2). The appreciable negative values of ϕ_k^0 suggest the existence of ion-solvent interaction[14]. The negative values may be due to a loss of compressibility of the solvent due to strong electrostrictive forces of ions. The corresponding S_k values are found to be positive for potassium sulphate and negative for potassium chloride which indicates the presence of ion-ion interaction. From the magnitude of ϕ_k^0, it is concluded that potassium sulphate is more compressed than potassium chloride. The ϕ_v values are positive for both the systems studied and its variation was not uniform. Comparing the values of ϕ_v, the magnitude of potassium sulphate (table 1) is greater than that of potassium chloride solution. This variation represents the existence of strong ionic bonding between solute and solvent molecules in potassium sulphate solutions compared to potassium chloride solutions. The volume behaviour of a solute at infinite dilution is satisfactorily represented by (ϕ_v^0) which is independent of ion-ion interaction and provides information regarding solute-solvent interaction. Since (ϕ_v^0) has been regarded as a measure of solute-solvent interactions by many workers[15-17], greater magnitude of (ϕ_v^0) in a solution may be considered quantitatively as a measure of greater solute-solvent interactions. From the perusal of table 2, ϕ_v^0 is positive for both the systems whereas the magnitude is greater for potassium sulphate which further confirms that the molecular association is greater in this system than potassium chloride. The S_v value shows the existence of ion-ion interaction. Viscosity is also an important parameter in understanding the structure and molecular interaction occurring in the solutions and its variation is attributed to the structural changes. Table 2 shows that the values of A are negative and B-coefficient are positive in both systems. A is a measure of ion-ion interaction and it is evident that there is a weak ion-ion interaction in the systems. B-coefficient is also known as measure of order or disorder introduced by the solute into the solvent. It is also a measure of solute-solvent interaction and the relative size of the solute and solvent molecules. The B-coefficient is greater in magnitude for potassium sulphate suggests the existence of strong solute-solvent interaction than potassium chloride. The large positive values of B coefficient support the behaviour of ϕ_v^0 and the dominance of solute-solvent interactions over solute-solute interactions[18]. Further, larger values of B indicate the structure making capacity of the solute[19]. The positive B coefficients suggest kosmotropes (structure-making) because strongly hydrated solutes exhibit a larger change in viscosity with concentration whereas negative B coefficients indicates chaotropes (structure-breaking) for weakly hydrated solutes[20]. The molar solvated volume ϕ_s measures the volume of solvated part of the solute present in the solution. The ϕ_s values have the cumulative effect of ϕ_v and $n_h V_1$ as seen from the equation (7). From fig. 5, it is clear that ϕ_s is mainly detailed by the hydration number rather than by ϕ_v in both the systems. From the magnitude, it is confirmed that molecular association is greater in potassium sulphate than potassium chloride.

V. CONCLUSION

The density, viscosity and ultrasonic velocity of aqueous potassium chloride and potassium sulphate solutions were measured at 303K. Using these datas, hydration number, apparent molal compressibility, apparent molal volume, molar solvated volume, and viscosity B coefficient were calculated to explain the solute-solvent and solute-solute interactions existing in the solutions. From the magnitude of ϕ_k^0, ϕ_v^o and of B coefficient, it was found that molecular association is dominant in potassium sulphate than potassium chloride solutions.

Table 1   Adiabatic compressibility (β), molal hydration number (n_h'), apparent molal compressibility (ϕ_k), apparent molal volume (ϕ_v), molar solvated volume (ϕ_s) of potassium chloride (KCl) and potassium sulphate (K$_2$SO$_4$) at 303K

Molality (m)	Adiabatic compressibility (β) (10^{-10} m^2 N^{-1})	Molal hydration number (n_h')	Apparent molal compressibility (ϕ_k) (10^{-8} m^2 N^{-1})	Apparent molal volume (ϕ_v) (m^3 mol^{-1})	Molar solvated volume (ϕ_s) (m^3 mol^{-1})
Potassium chloride					
0.10	4.3499	14.1524	-10.1144	28.5328	254.9651
0.15	4.2792	15.2920	-11.3052	22.3360	275.4966
0.20	4.2572	12.839	-9.31776	22.6403	231.3032
0.25	4.22264	11.8049	-8.38769	24.8312	212.6738
0.30	4.2080	10.5978	-7.30666	27.2918	190.9271
0.35	4.1778	10.1567	-6.90635	28.3058	182.9806
Potassium sulphate					
0.10	4.2750	23.4734	-16.2116	59.7175	422.8972
0.15	4.2033	21.5923	-16.1184	27.9125	389.0062
0.20	4.1396	20.1565	-14.7276	33.2027	363.1391
0.25	4.0952	18.3332	-13.0228	38.5479	330.2908
0.30	4.0588	16.7840	-11.336	48.4253	302.3809

0.35	3.8314	22.4677	-16.6409	31.9783	404.7774

Table 2   **Limiting apparent molal volume (ϕ_v^o), limiting apparent molal compressibility (ϕ_k^o), constants S_v, S_k and viscosity A and B coefficients of Jones-Dole equation for potassium chloride (KCl) and potassium sulphate (K$_2$SO$_4$) at 303K**

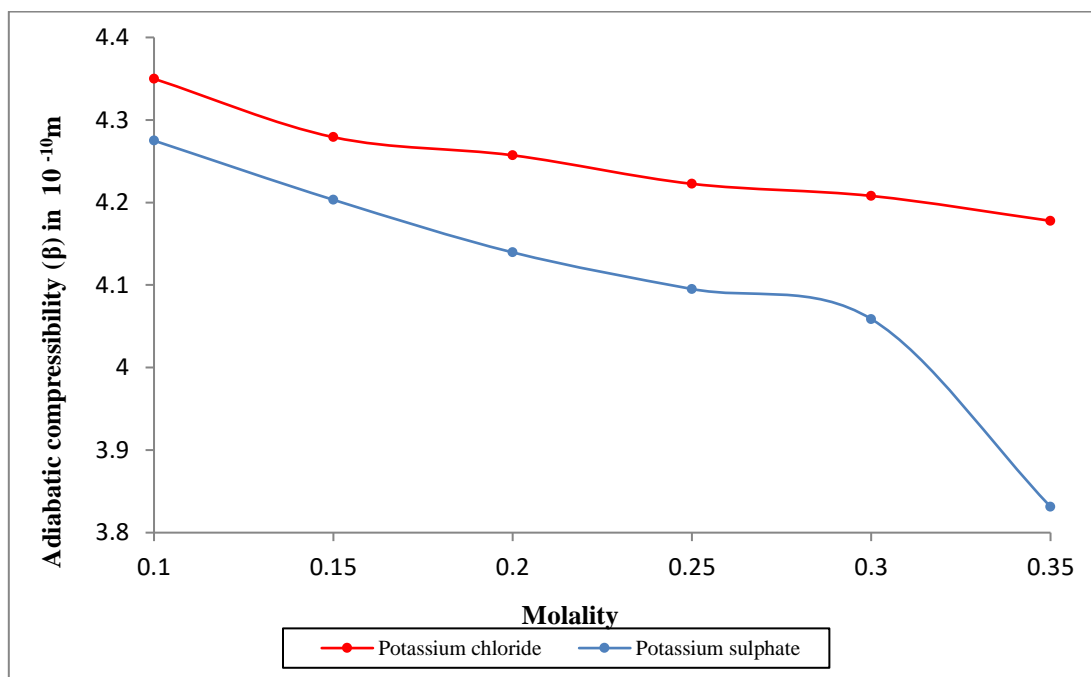| System	ϕ_v^o m^3 mol^{-1}	S_v m^{-1}N^{-1} mol^{-1}	ϕ_k^o in 10^{-8} m^2 N^{-1}	S_k in 10^{-8} m^{-1}N^{-1} mol^{-1}	Viscosity coefficient	
					A dm$^{3/2}$ mol$^{-1/2}$	B dm^3 mol^{-1}
KCl	22.7809	6.1834	-6.7214	-4.6628	-0.1579	0.1303
K$_2$SO$_4$	59.7771	-42.5981	-18.4467	8.1067	-0.0730	0.1791

Fig 1   **Adiabatic compressibility of potassium chloride (KCl) and potassium sulphate (K$_2$SO$_4$) at 303K**
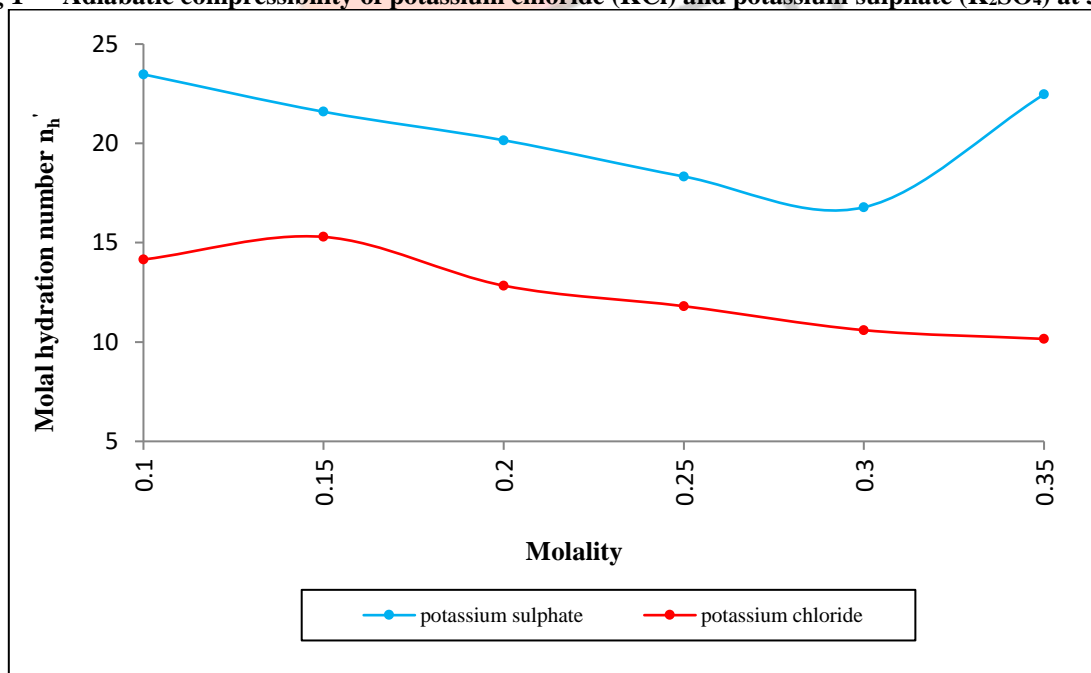

Fig 2   **Molal hydration number of potassium chloride (KCl) and potassium sulphate (K$_2$SO$_4$) at 303K**
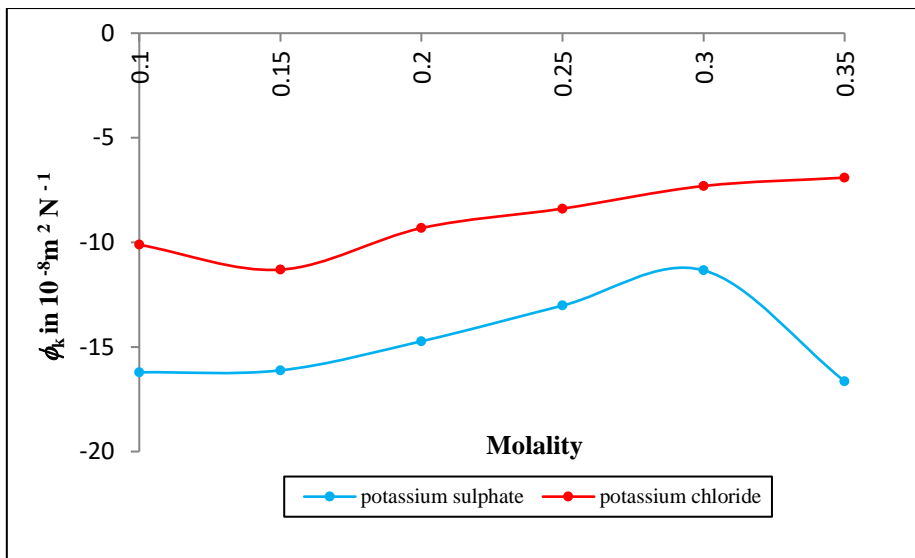
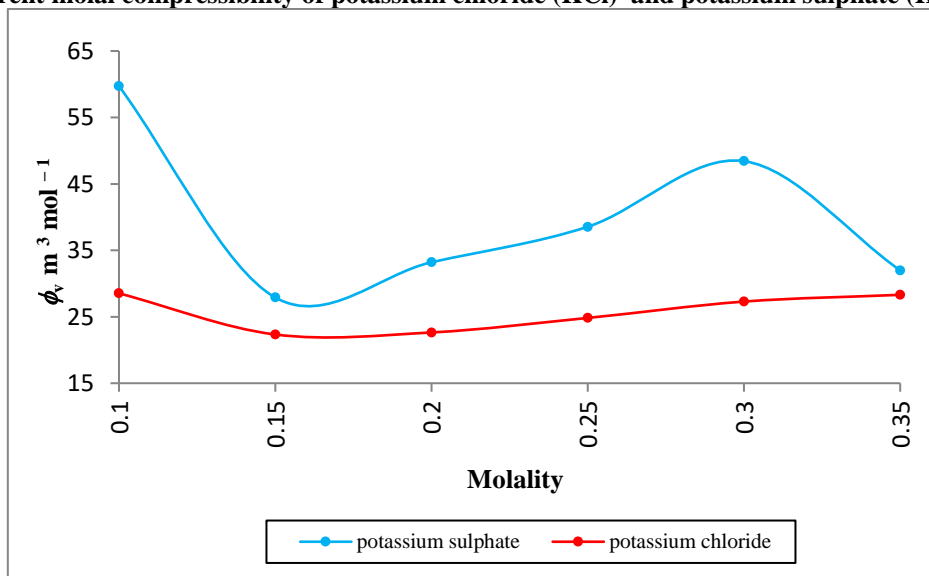**Fig 3   Apparent molal compressibility of potassium chloride (KCl) and potassium sulphate (K$_2$SO$_4$) at 303K**

Fig 4   Apparent molal volume of potassium chloride (KCl) and potassium sulphate (K$_2$SO$_4$) at 303K
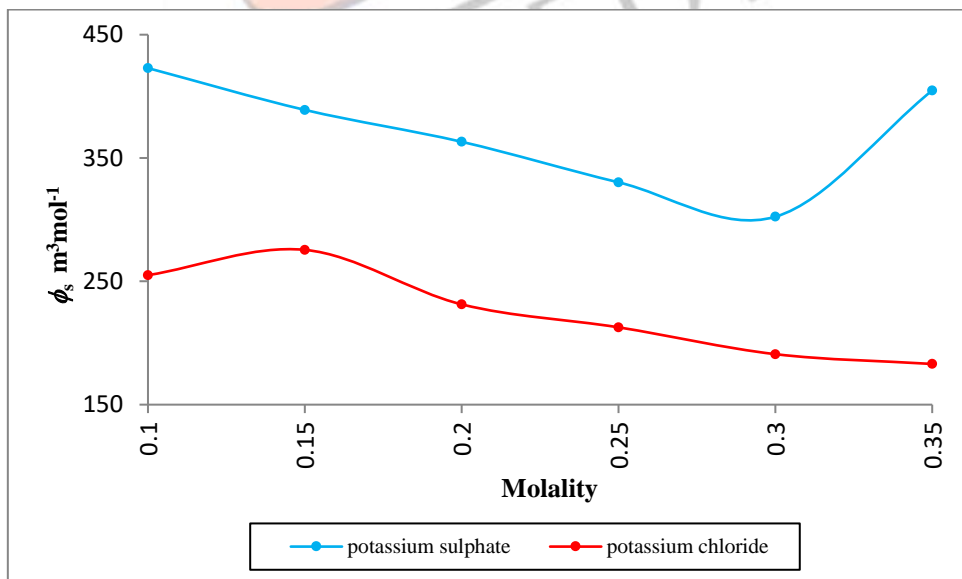

Fig 5   Molar solvated volume of potassium chloride (KCl) and potassium sulphate (K$_2$SO$_4$) at 303K

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