Original Research Article

STRUCTURE MAKING AND BREAKING EFFECTSOF MOLIONIC AQUEOUS SOLUTIONS ESTIMATED WITH DENSITY, APPARENT MOLAL VOLUME, SURFACE TENSION, VISCOSITY, FRICCOHESITY, ACTIVATION ENERGY AND ENTROPY AT 293.15 K

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Abstract:
Density, apparent molal volume, surface tension, viscosity and friccohesity data for 0.01 to 0.1 mol activities at surface and bulk respectively. Viscosity, friccohesity and apparent molal volume kg^{-1}aqueous $K_2Cr_2O_7$, K_2HPO_4, $KMnO_4$, KH_2PO_4, KCl and KOH at an interval of 0.01 at 293.15 K are studied. Surface and bulk chemical potentials determined from surface tension to analyze ionic data were used to calculate intrinsic viscosity, viscosity B coefficient, intrinsic friccohesity and activation energy as well as entropy changes. Limiting density, surface tension and viscosity obtained by fitting Redlich–Kister equation for ionic contribution onion-water interactions (IWI). Limiting surface tension and B data plotted with intrinsic friccohesity slopes that inferred a reverse relation between surface tension and B coefficient related to cohesive (CF) and frictional forces (FF) on account of surface energy and hydration dynamics respectively. The CF and FF forces are opposite and reinforced with anionic sizes for surface tension and B behavior. Activation energy and entropy data revealed spontaneous interaction of chosen salts with water that inferred structure breaking and making activities.

Keywords: Ion water interaction, ionic size, surface tension, intrinsic viscosity, cohesive, frictional

Introduction

For a long aqueous ionic liquids (AILs) have drawn attentions of researchers being a most efficient and effective medium for several chemicals, biochemicals, biotechnological, biophysical, nutritional and food sciences[1]. AILs

are popularly used as catalysts in synthesis and other industrial processes of drugs and materialsdesigning[2, 3]. Their anionic constituents are noted as most useful parts of the salt solutions to induce and introduce catalyzing, solubilizing, salting out, phase separate on liquid-liquid interfaces and extractions for pharmaceutical uses by solvation processes[4, 5]. At lower ionic concentration, the AILs could be useful where the viscosity and surface tension predict quality of ink and honey industries[5]. Each ion does induce its own effect on AIL and depicted with several physicochemical

indicators (PCI)for interacting activities as prerequisite requirements for industrial uses[6]. Their density, surface tension and viscosity are basic PCIs elucidate molecular-ion interaction as molionic dynamics. Studies of IWI at low concentrations have revealed that the molecules and ion-ion-interaction (III)play an important role for many phenomenon ranging from a hydrogen bond dynamics to water interfaces. Classical and abinitio molecular dynamic simulation have been reported induced-dipole movement development at interaction interfaces in support a concept of the molionic models to be implemented in classical force fields due to electrostatic properties[7]. The surface tension and viscosity studies reported by previous workers on several binary and ternary mixtures have been found an IWI in solvation processes as useful tools where a concentration dependence of viscosity was understood. Also in 1929, Jones and Dole suggested an empirical equation for concentration dependence of viscosity with $(\eta_2/\eta_1-1)/\sqrt{m} = A + B\sqrt{m}$ relation[8]. The A and B are empirical constants, thenη_1 and $\eta_2$as viscosities of solution and solvent respectively and m solute concentration. The $(\eta_2/\eta_1-1)/\sqrt{m}$ at m →0 is noted intrinsic viscosity as function of shape and size of participating molecules. Jones and Dole coefficient 'A' shows stiffening effect on III with ion-interaction force (IIF) calculated with ionic interaction theory[9]. The B reflected the IWI for a wide range of aqueous electrolytes and non-aqueous solvents for structural changes[10-11]. A little later, Falkenhagen and Dolet had attempted to resolve such complications theoretically using ion-atmosphere Debye and Huckel theory[9]. The B value is negative when the viscosity of AIL is less than of the water while it is positive for highly polarizing ions due to salt structure making or breaking actions as studied by Frank and Wen[11]. For example, aqueous potassium, rubidium and cesium chloride salts solutions exhibited negative η due to less viscous than pure water[12]. The surface tension is very sensitive with charge accumulation on anionic group and higher than pure water with salt contribution at low concentration[13, 14]. The

structural interactions are governed by so many factors like ionic sizes and charges along with metallic anions responsible for chemical changes such as structure breakers or makers that potentially disrupt water structure. The viscosity and surface tension act as authentic PCI for several industrial processes for developing applications with interesting insights on type and nature of solvation and structural interactions for better understanding of any individual chemical process[15,16]. The electrostatic properties of hydrated and metallic anions are depicted with variations PCIs where the CF and FF function either separately or together to elucidate strengths of hydrogen bonding and ion polar interaction (IPI).The study developed new models for strong electrolytes at lower concentration for applications and science being used in molecules or complex compounds of transition metals[17].

Experimental section

Chemicals (AR, 99.99% $K_2Cr_2O_7$, K_2HPO_4, $KMnO_4$, KH_2PO_4, KCl, KOH Ranbaxy, India) were used as received. Solutions were prepared w/w, using Mettler Toledo electronic Kern balance ABS 220-4 model with ± 0.01 mg accuracy. Densities were measured with ± 10^{-3} kg m^{-3}accuracy by Anton Paar Density and Sound velocity meter DSA 5000 M that works based on oscillation periods of quarts U tube with air, solvent and solutions[18]. The meter was calibrated with water and dry air as per the manufacturer's instructions (DMA instruction manual; Anton Paar, Graz, Austria). A process of drying was continued till a constant oscillation period for air was obtained and noted as an initial calibration. The pendent drop numbers (PDN) and viscous flow times (VFT) were measured with Borosil Mansingh Survismeter (BMS) for surface tension and viscosity measurements respectively[19]based on a socket and cone model (SAC). The BMS is a multidata measuring device enabling measurements of both the PDN and VFT together with single instrument. For a temperature control, an auto temperature control LAUDA ALPHA RA 8 thermostat was used for T = 293.15 K with ± 0.010C accuracy. Almost

15 to 20 measurements were repeated for a single sample for ensuring high accuracy and precision. The PDN and VFT methods for measurements of surface tension and viscosity respectively were used as reported in literature using BMS[19]. For the pendent drop formation, the fluid flows in surface tension capillary of BMS from top to downward where frictional forces are operational within rigid and uniform capillary. At the end of capillary, the solid surface of capillary has vacant force which develops a solid-liquid interface and operationalized by adhesive force to assist an unaltered pendent drop formation. For constant volume, the PDN were counted. For the measurement of VFT, the liquid was filled in viscosity capillary attached with surface tension capillary in BMS, and for constant volume it was measured. The PDN and VFT were used to calculate surface tension and viscosity respectively, as mentioned in result and

discussion section. The SAC is applied alternatively, for example, for surface tension measurements the cone was fitted with viscosity unit and vice versa.

Results and discussion

Density, surface tension, viscosity, apparent molal volume, viscous flow energy and entropy changesas physicochemical indicators

Densities (ρ) for molionic aqueous solutions $K_2Cr_2O_7$, K_2HPO_4, $KMnO_4$, KH_2PO_4, KCl and KOH from 0.01 to 0.1 mol kg^{-1} with an interval of 0.01 at 293.15 K have been critically interpreted. For example, the densities have increased with concentration of the salts as their compositions have strengthened the IWI by causing higher internal pressures with higher densities. Densities were used to calculate surface tension and viscosity with equations 1 and 2 respectively[19].

$$\gamma = \gamma_0 \left(\frac{n_0}{\rho_0} \right) \left(\frac{\rho}{n} \right) \qquad (1)$$

$$\eta = \frac{\eta_0}{\rho_0 . t_0} \rho . t \quad (2)$$

The γ_0, ρ_0 and n_0 are surface tension, density and drop number of water while ρ and n are density and pendant drop number of salt solutions respectively. The η_0 and t_0 are viscosity and viscous flow time for water respectively while t is a viscous flow time for salt solutions. The surface tension is a cohesive property where the molecules or particles sustain their cohesivity with a uniform molecular arrangement in liquid. Similarly, on developing interaction, the water molecules surround the cations and anions by forming an intimate ion pair process depicted by viscosity[20]. Initially, the ions disrupt the water structure as their structure breaking action while the molecules regain and catalysed by the ions to surround them for developing ion hydration as a specific state function. On an increasing salts concentration, the surface tensions and

viscosities have increased inferring that numbers of the ions favor a development of interactions atmosphere. Surface tension and viscosity with the salts concentrations have varied due to, salt's composition effect on IWI. The increase in surface tension with concentrations for chosen salts inferred a weakening of structured thin film at their air liquid interface. It reflects a formation of hydration spheres (HS) salts developed stronger interaction with water due to stronger IPI forces. It depicts a role of cationic aggregation on surface with salt concentration and has been used for determining a colloidal dynamics of several systems[21]. The variation in surface tension and viscosity of salts with compositions furnish useful information about the salts solutions of biological significance for conducting the desired biochemical process without any interference and in providing

physicochemical support. The limiting density (ρ^0) and surface tension (γ^0) are noted as KCl > KH_2PO_4 > $K_2Cr_2O_7$ > KOH > K_2HPO_4 > $KMnO_4$ with structurally stronger interactive with the KCl and the weaker with $KMnO_4$. This inferred stronger effect of Cl^- than of the MnO_4^- on interactions. It seems that an impact of internal pressure also influenced the surface energy by creating stronger down pull with stronger CF due to stronger ionic interaction (Fig.1). Since the Cl^- is a single atom anion and increased the pair wise interaction (PWI) with increase in concentration (m). Thus, the K^+ and Cl^- developed HS separately along with their interactions. The HS of the K^+ and Cl^- have equally contributed to increase compactness due to smaller size and similar structures. Both the HS interacted to each other due to different electronic environments with stronger hydration sphere interactive forces (HSIF) pulling down surface with an additional CF depicted in Fig. 1.The difference in sizes of OH^- and water molecule is due to only of the H^+ so due to similarity in nature of OH^- and water except size, their interaction produced stronger CF and increased the surface tension. Thereby, a new force formulation model for explanation of the surface tension of AILs is proposed as under.

$$CF = FE + HSIF \qquad (A)$$

The FE is fundamental electronic configuration and the γ^0 inferred a stronger cohesion with KH_2PO_4 than K_2HPO_4(Fig. 1) where the K^+ numbers also contributed to generate CF. Infect, the PO_4^{-3} has equally contributed to water in both salts where the H^+ and K^+ act as cohesive factors. The H^+ is effective to bind the disperse water molecules together and acts as linker while the K^+ formed two cation hydration spheres (CHS) which repulsed each other due to the same electronic environments and produced comparatively lower CF for the K_2HPO_4. Thus, comparing $K_2Cr_2O_7$ with the K_2HPO_4 showed no effect of CHS but the size of $Cr_2O_7^{--}$ is larger than of HPO_4^{--} and hence the K_2HPO_4 has weaker CF than $K_2Cr_2O_7$ with strong pulling surface (Fig. 1). The size of MnO_4^- is larger than HPO_4^{--} but the CF is stronger with the K_2HPO_4 due to an only one position is available for interaction in MnO_4^- while in the HPO_4^{--} the three positions are available for interactions and one H^+ is also at interactive position. Thus, the IWIF is stronger with the HPO_4^- andalso developed a unique model based on interacting positions with either negative charge or the positive charge on the ions subjected for study. Thus model A may be modified as model B.

$$CF = FE + HSIF + IP \qquad (B)$$

The IP is interactive position and γ slopes 14.103, 10.964, 7.937, 6.624 and 2.981 are as $K_2Cr_2O_7$ > K_2HPO_4 > $KMnO_4$ > KH_2PO_4 > KOH > KCl respectively, which inferred maximum composition effect (CE) of $K_2Cr_2O_7$ while minimum of the KCl on CF responsible for surface tension. Thus, the factors such as anionic sizes, numbers of the CHS and free hydrogen atoms are responsible for stronger CE with higher CF magnitude. Hence a largest anionic size, 2 CHS with a tri hydrated anion and anionic size of $K_2Cr_2O_7$, K_2HPO_4 and $KMnO_4$ respectively induced them compositionally most interactive. Thereby, the positive slopes inferred stronger CE on the CF and model B may referred as C to incorporate the CE.

$$CF = FE + HSIF + IP + CE \qquad (C)$$

Contrary to surfactants a surface accumulation of salts is least with varying surface activities due to surface energy or tension, and hence the surface (μ^S) and bulk chemical potentials (μ^B)

were calculated with surface tension data using

equations 3 and 4 respectively as under.

$$\mu^{S} = \mu^{0} + RT \ln \tau_{s} \qquad (3)$$

$$\mu^{B} = \mu^{0} + RT \ln \tau_{B} \qquad (4)$$

The surface concentration (τ) is analyzed with equation 5.

$$\tau = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln c}\right) \qquad (5)$$

R gas constant, T temperature, $\partial\gamma = \gamma_{\text{solvent}} - \gamma_{\text{solution}}$ and c is concentration (m). The μ^{S} are found as $K_2Cr_2O_7$ > $KMnO_4$ > K_2HPO_4 > KH_2PO_4 > KCl > KOH while the μ^{B} as KOH > KCl > KH_2PO_4 > K_2HPO_4 > $KMnO_4$ > $K_2Cr_2O_7$ (Fig. 2) with a reverse behavior respect to anionic size. The μ^{S}/μ^{B} ratios are as 1.36:1, 1.43:1, 1.43:1, 1.52:1, 1.64:1 and 1.69:1 respectively to μ^{S} and μ^{B} trends infer that large sized anion $Cr_2O_7^{--}$, PO_4^{-3} and MnO_4^{-} showed weaker interaction while the KCl and KOH with no covalent bonding forces showed

stronger interaction. Salts did not get accumulated at surface but still show mild activities by pulling down or dispersion mechanism and their trend inferred a cohesive activity at surface and bulk. In bulk a cohesive activity of solvent or water molecules is less than surface activity because at surface two types of attraction forces are workable first the air liquid forces at upwards and liquid-liquid forces downwards. The size dependent intrinsic viscosity [η] is calculated with Jones Dole equation as under.

$$\frac{(\eta_{r} - 1)}{\sqrt{m}} = A + B\sqrt{m} \qquad (6)$$

The $\eta_{r} = \eta_{\text{soln}}/\eta_{\text{solv}}$ relative viscosity, the A and B are coefficient. The $(\eta_{r} -1)/\sqrt{m}$ at m→ 0 is intrinsic viscosity [η]. The Jones and Dole equation's 'A' and B coefficients were derived from polynomial equations of [η] vs $\sqrt{m}$ (Fig 3). The viscosity 'A' coefficient depicted the III as KH_2PO_4 (0.3296) > KCl (0.1559) > $K_2Cr_2O_7$ (0.0746) > KOH (-0.0047) > $KMnO_4$ (-0.0449) > K_2HPO_4 (-0.1233) with decreasing strength of their Columbic attractions or disruption of Columbic force. Their positive and negative values inferred the weaker and stronger disruptions of Columbic forces respectively with stronger interacting activities due to a stronger IPI. Thus, the KH_2PO_4, KCl and $K_2Cr_2O_7$ with positive 0.3296, 0.1559 and 0.0746 $kg^{1/2}mol^{-1/2}$ A values respectively showed stronger III while KOH, $KMnO_4$ and K_2HPO_4 with negative -

0.0047, -0.0449 and -0.1233 $kg^{1/2}mol^{-1/2}$ A values respectively showed weaker III. The coefficient B is noted as K_2HPO_4 > $KMnO_4$ > KOH > KCl > $K_2Cr_2O_7$ > KH_2PO_4 due to stronger IWI with K_2HPO_4 while the weaker with KH_2PO_4 with 3.819 kg/mol difference. The B values inferred an effect of ionic influence on the water structure where the K_2HPO_4 (2.229), $KMnO_4$ (0.830) and KOH (0.235) showed positive B values with stronger ion-water bindings than of the water-water itself which constitutes a less entropic structure due to orderedness in ion-water structures. Thus, the K_2HPO_4, $KMnO_4$ and KOH with 2.229, 0.830 and 0.235 kg/mol behaved as structure makers while the KCl, $K_2Cr_2O_7$ and KH_2PO_4 with -0.716, -0.799 and -1.59 kg/mol negative values as structure breakers. Conceptually, the ionic

size contributes to B values where the stronger and weaker IWI of the K_2HPO_4 and KH_2PO_4 respectively caused opposite contributions to structural interactions by 3.819 kg/mol. There placement of an H^+ from potassium hydrogen phosphate salt caused a critical salt - water interaction with higher contribution of K_2HPO_4 due to K^+. Thus, the cations matter a lot towards a maker effect on the water while the KH_2PO_4 with only 1 K^+ caused a breaking effect. Thus, the K_2HPO_4-water interactions are 2 times stronger than of the KH_2PO_4 with 2 times higher structure making effect as compared to breaking effect of the KH_2PO_4. The ratio of their B values are 1.4:1.00 derived from $(K_2HPO_4)/(KH_2PO_4)$, with 2.8 times higher structure making effect than breaking effect of KH_2PO_4. Similarly with $KMnO_4$ the IWI is stronger than $K_2Cr_2O_7$ because the Mn and Cr metals are in +7 and +6 oxidation states. Thereby, the MnO_4^- interacted strongly as compared to $Cr_2O_7^{--}$ due to much electrophilic environment where the B values are in 1.62:1 ratio, higher as compared to $(K_2HPO_4)/(KH_2PO_4)$ by 1.4:1.00. Also probably 2 Cr (+6) developed 2 times more HS due to inter-hydration spheres interaction with competitive Cr (+6) and Cr (+6) HS structure as compared to MnO_4^- with single Mn (+7). The higher B value of the MnO_4^- than $Cr_2O_7^{--}$ by 1.55 kg/mol depicted stronger structure making while the latter as breaker. The mechanism could be that the K^+ and MnO_4^- fundamentally developed 1: 1 cationic and anionic HS respectively while the $2K^+$ and $Cr_2O_7^{2-}$ the 2:1. Thus, the 1:1 is most effective in disrupting water structure and making stronger bond with monomer water. The highest B value was with K_2HPO_4 with development of HS in 2:1 rations which inferred that ratios of the hydration spheres decide a structure making and

breaking activities. Thus, the K_2HPO_4 disrupted bulk water in larger extent and water disrupting strength decreased due to hydration ratios. Thus, the number of the K^+ in combination of specific anionic structure influenced hydrogen bond disruption. Probably H^+ also released from HPO_4^{--} and $H_2PO_4^-$ which could also constituted a HS in interaction. The B values are as $HPO_4^{--}>$ $H_2PO_4^-$ by 3.819 kg/mol as their H^+ are released in 1:2 ratio interestingly a most useful information that when a cationic of least size that is H^+ are in 1:2 ratio than the molecule which released ½ of the another developed slightly stronger structure makers. Although, the H^+ ion may not be able to develop a HS around the H^+ on a pattern of cation but is able to interact with the dipolar water where the interacting behavior of the H^+ of K_2HPO_4 and KH_2PO_4 have confirmed the same behavior. Thus, the number of K^+ and H^+ of their respective salts are noted to monitor the water structure making or breaking activities. Notably, the KOH developed a stronger IWI due to almost similar nature and sizes of OH^- and H_2O. Also, the KCl with compatibility in size, their HS interacted mutually due to opposite electronic environments. The B values of KOH and KCl are in 1.95:1.00 ratios where the structure making effect of the KOH is 1.95 times higher than breaking effect of KCl. The trends of coefficient 'A' and B values are opposite except the $K_2Cr_2O_7$ and KCl due to different workable forces associated with their ionic charges. In III opposite charge ionic force or Columbic force but in IWI the IPI or IWIF are workable. Noticeably, an increase in γ^0 as a function of the CF, the B values as a function of FF have decreased except K_2HPO_4 and KCl. To analyze such behavior of salts the friccohesity[22] was calculated as under.

$$\sigma = \sigma_0 \left[\left(\frac{t}{t_0} \pm \frac{B}{t} \right) \left(\frac{n}{n_0} \pm 0.0012 (1 - \rho) \right) \right] \qquad (7)$$

Similarly, intrinsic friccohesity $[\sigma]$ is calculated as under where $\sigma_r = \sigma_{soln}/\sigma_{solv}$ is relative friccohesity.

$$[\sigma] = \left(\frac{\sigma_r - 1}{\sqrt{m}} \right)$$

The γ^0 and B values were plotted with $S_{[\sigma]}$ depicted in Fig.4 where a most fascinating feature of the KOH is noted that the γ^0 and B values are intersecting at -1.45 kg mol^{-1} $S_{[\sigma]}$. It inferred almost the same operational strengths of CF and FF, may be due to $4s^0$ and most electronegative O of the OH$^-$.The γ^0 showed a sigmoid curve with $S_{[\sigma]}$ and B an almost linear line inferred the FF with solute-solvent interaction increased from KH_2PO_4 <$K_2Cr_2O_7$ <KCl < KOH < $KMnO_4$<K_2HPO_4 with increase in the $S_{[\sigma]}$ from -4.50 to 1.50 kgmol^{-1} values. The latter inferred that with increase in the $S_{[\sigma]}$, the B values have increased or the solute-solvent interactions have strengthened due to FF. The γ^0 with KCl > KH_2PO_4 > $K_2Cr_2O_7$ > KOH > K_2HPO_4 > $KMnO_4$ and the B with the K_2HPO_4> $KMnO_4$>KOH> KCl> $K_2Cr_2O_7$>KH_2PO_4 sequence developed cross relationship in their CF and FF with product of the FF and CF as friccohesity. Remarkably the Fig.4 showed a reverse relation in CF and FF of KH_2PO_4, KCl, $K_2Cr_2O_7$, KOH, $KMnO_4$ and K_2HPO_4on their own comparison respectively. Thus, the CF and FF showed an opposite relationship of each salt with lower gap of KOH and when the γ^0 and B values were plotted with anionic sizes then also a reverse relation noticed in CF and FF (Fig. 4).The one metallic anion produced higher B value than two metallic anions such as in $KMnO_4$ and $K_2Cr_2O_7$ respectively. The $KMnO_4$ and $K_2Cr_2O_7$ have Mn^{7+} and Cr^{6+} anionic metals noted as one metallic and two metallic anions respectively. It reveals an interesting correlation between oxidation numbers and the CF and FF whereby Mn^{7+} with higher oxidation has produced higher B values than Cr^{6+} with lower oxidation number. Further the oxidation numbers are also supporting a historic relationship between the CF and FF with opposite values of the B and the γ^0 depicted in Figure 4. Hence the salts with metallic ion with higher oxidation number have also developed a stronger FF and weaker CF while the ion with lower oxidation numbers showed a reverse interacting activity considering CF and FF. Thus, the CF and FF producing capabilities of salts could be excellently analyzed with friccohesity a new and historic phenomenon determined with Survismeter. Such valuable data could be most useful in academics and industries to design mixtures of desired CF or FF as an urgent or fundamental requirement of specific chemical or pharmaceutical processes. Though, the γ is a surface energy for per unit area as function of CF while the B is as of IWI. Thus, the $K_2HPO_4$with strongest IWI and has highest FF and the KCl with highest CF caused weaker IWI. The KH_2PO_4depicted weakest IWI and the $KMnO_4$the weakest cohesion so the FF dominates over the CF with K_2HPO_4. Thus, the CF and FF are constitutionally separate forces and operational in γ and η respectively. Thus, the friccohesity is a unique phenomenon and differentiated the dominancy of CF and FF in IWI including dipolar interacting forces and is depicted as under.

$$\sigma = M_c \left[t_{water}\, n_{water}\, x_{water} + t_{salt}\, n_{salt}\, x_{salt} \right]$$

The t depicts viscous flow time, n pdn and x the mole fraction. Theoretically it elucidates a science of the interconvertibility of operational forces during fluid dynamics and practically conceptualizes a dual force theory in aqueous ionic liquids visa-s-vise III. Thus notably the similar trends of [σ] and [η]due to mutual distribution, sharing or diversification of the ionic forces which explain and elucidate a probable structural mechanism depicted with the η and γ in coexistence. With the η, the FF operated over fluid dynamics but with the σ both the FF and CF operated to elucidate and distinguished unification, diversification and accumulation of the operational forces during fluid flow. The different magnitude of both the η and σ, predicted a conversion of IWIF into CF and FF. Thus, the σ is an additional account of CF and FF as direct function of electronic configuration and dipole movement. For the η calculation a statistic property density is must while the σ does not require and act as operational force in itself. Apart from B values,

apparent molal volume, $V_2^{*\#}$, calculated as under

and studied.

$$V_2^{*\#} = 1000\left(\frac{\rho_0 - \rho}{m.\rho.\rho_0}\right) + \frac{M}{\rho} \qquad (8)$$

The m and M are molality and molecular weight of salt solutions and salts respectively. The $V_2^{*\#}$ is immensely used in aquatic environmental, in biochemical sciences for determining molecular weight, unfolding of proteins and nucleic acids using ultracentrifugation[23]. Since, the ultracentrifugation depends on a size of the particles as the size of the Na^+ and K^+ hydration spheres, and hence the efficacy and unfolding of the protein and deformation in DNA could be

studied. The $V_2^{*\#}$ data explained ionic interactions which elucidated a net concentration effect on the cationic interactions. The positive $V_2^{*\#}$ values varied with concentrations of salts on involving interacting energy. Thus, a concentration dependence change in free energy ∂G at constant pressure and temperature is obtained as under.

$$\partial G = \left(\frac{\partial G}{\partial n_1}\right)n_2 \, \partial n_1 + \left(\frac{\partial G}{\partial n_2}\right)n_1 \, \partial n_2$$

The $\left(\frac{\partial G}{\partial n_1}\right)n_2 \, \partial n_1$ and $\left(\frac{\partial G}{\partial n_2}\right)n_1 \, \partial n_2$ are changes in free energy per mol[23]. A contribution of salts for free

energy, $\Delta\mu_2^{\#}$, of viscous flow and entropy are calculated with equations 9 and 10 respectively.

$$\Delta\mu_2^{\#} = RT \ln\left(\frac{\eta \, V_2^{*\#}}{h \, N_A}\right) \qquad (9)$$

$$\Delta S_2^{\#} = -\left(\frac{\Delta\mu_2^{\#}}{\Delta T}\right) \qquad (10)$$

The R = gas constant, T = temperature, η = viscosity, h = plank constant and N_A= Avogadro number. The $\Delta\mu_2^{\#}$, $\Delta S_2^{\#}$ are thermodynamic functions and elucidate a solute (salts) effect on structure of the solvent with solute-solvent interactions. The salts have produced the negative $\Delta\mu_2^{\#}$ values because the salts have

interaction spontaneity with stronger spontaneity with structural interaction. According to Feakins et. al., the $\Delta\mu_2^{\#}$ reveals that the solute and surrounding solvent molecules interactions with a movement of solute molecules through a transition state[11], is represent as equation 11.

$$\mu_2^{\#} = \mu_2^{\#}\left(1 \rightarrow 1^*\right) + \mu_2^{\#}\left(2 \rightarrow 2^*\right) \qquad (11)$$

The $\mu_2^{\#}\left(1 \rightarrow 1^*\right)$ represents a solute contribution for $\Delta\mu_2^{\#}$ of solvent, and the $\mu_2^{\#}\left(2 \rightarrow 2^*\right)$ is stay for the $\Delta\mu_2^{\#}$ of solute itself. The $\Delta\mu_2^{\#} < 0$ inferred spontaneous interaction where a decrease in

$\Delta\mu_2^{\#}$ inferred a favorable process. The $\Delta\mu_2^{\#}$, B and $\Delta S_2^{\#}$ are correlated and depicted in Fig.5 whereas the $\Delta\mu_2^{\#}$ and $\Delta S_2^{\#}$ are as $K_2Cr_2O_7$ > K_2HPO_4 > $KMnO_4$ > KH_2PO_4 > KCl > KOH with having 1, 8, 6, 8, 2 and 3 atoms

respectively. It may cause higher degree of freedom with high entropy where the linear limiting entropies are rationalized (Fig. 5) with respect to KOH whose $\Delta S_2^{\#}$ are 1.08, 1.06, 1.05, 1.04 and 1.01 times lower with the $K_2Cr_2O_7$, K_2HPO_4, $KMnO_4$, KH_2PO_4 and KCl respectively. The $K_2Cr_2O_7$ entropy is highest with highly spontaneously process depicted with its activation energy, larger atoms number, repulsion between two CHSs and larger size of interacted $Cr_2O_7^{--}$. Hence, the $K_2Cr_2O_7$ with stronger compositional effect on interactions, the entropy is also higher that very much fitted in the natural trend. As the molecules with maximum activities the entropy is always higher than weaker interacting activities with composition such as KCl. The latter randomized the environment more than others with increase in entropy with higher water structure breaking capacity with higher negative B values. For K_2HPO_4, the entropy is higher due to two CHS and slightly higher interacting activities. The anion size of $KMnO_4$ is larger than K_2HPO_4 but lower entropy due to having only one CHS and interactive position. The K_2HPO_4 and KH_2PO_4 both have the same anionic sizes but with only one CHS, the KH_2PO_4 entropy is lower as there is no HS repulsion. The entropy and B values for $KMnO_4$ are between the K_2HPO_4 and KH_2PO_4 against their energy may be due to numbers of atoms are lower by 2 as compared to K_2HPO_4 and KH_2PO_4. It is related to their degree of freedom where larger numbers of the atoms caused higher degree of the freedom. In KCl, the K^+ and Cl^- are smaller in size that created milder random environment as compared to others. The KOH showed lowest entropy while the numbers of atoms are more than of the KCl where CHS numbers play key role to raise the entropy.

Conclusion

The study distinguished salt-water interactions even when MnO_4^-, $Cr_2O_7^{--}$ anions with transitional metal is present with K metal for anionic contributions. The CF = FE + HSIF+ IP + CE model is proposed as a cutting edge input as compared to routine models. The viscosity A coefficient inferred III in routine but our study correlated the A with degree of disruption in Columbic force. The B ascertained solute contributions and reorient solvent structure along anionic sizes which induced anionic interacting capacity of solvent binding with many interactive positions in anion like MnO_4^- and $Cr_2O_7^{--}$. The salts-solvent along the HS interaction is found responsible for CF whereas the HS repulsion influenced the FF and entropies. Thus Ion Hydration Spheres Interaction and Repulsion (IHSIR), noted as a new theory was evolved out of analysis applicable to distinguish PCIs properties of the salts. With the IWI, the FF is shared with the CF in form of the σ product. The γ values after 0.04, 0.05, 0.06 and 0.08m with the $K_2Cr_2O_7$, K_2HPO_4, $KMnO_4$ and KH_2PO_4 respectively noted as activation in terms of IWI and were higher than water however, initially were lower. The activity of CF and FF in context of IWI environment was critically investigated with CHS as functions of the CF and FF.

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