

Study of apparent molal volume and viscosity of mutual citric acid and disodium hydrogen orthophosphate aqueous systems

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Abstract. Fundamental properties, density (ρ) and viscosity (η), of citric acid (CA) and disodium hydrogen orthophosphate (DSP) at various strengths were obtained at different temperatures. The ρ and η values were used to determine apparent molal volumes and viscosity of systems. The ρ , V_f and η values were regressed against molality m for ρ^0 , η^0 and V_f^0 , the limiting constants at infinite dilution ($m \rightarrow 0$) for ionic and molecular interactions. The ρ^0 and V_f^0 of aq. acids are higher than those of aq. DSP and the viscosity of DSP is higher than that of aq. CA. Examination of ρ^0 and V_f^0 functions indicates that mutual compositions of CA and DSP counterbalance concentration and temperature effects on pH in bioprocesses.

Keywords. Citric acid–disodium hydrogen orthophosphate aqueous system; density/viscosity of aqueous systems; limiting constants at infinite dilution.

1. Introduction

Mutually citric acid (CA) and disodium hydrogen orthophosphate (DSP) have been useful buffers for studying biosystems,^{1,2} as physiological and biological activities are medium-dependent. Thus study of their interactions and physical characterization is essential. As per molecular modelling data, their interactions with water could influence actual biological processes and hence estimation of parameters such as density, volume and viscosity become necessary. CA and DSP are solvated in aqueous solution, occupying certain volume due to dipolar and ionic forces between them. This may have implications on the capacity and range of buffer usage. Also, CA is an important compound in cellular respiration for oxidizing glucose, fatty and amino acids and is related to acetyl coenzyme A of Krebs's cycle.³ Both CA and its conjugate base DSP of intra/extracellular fluids act as a first line of defence against changes of the internal pH.^{4–7} As molar expansion/contraction affects the interaction of buffers with biofluids/biochemicals, ρ and V_f data in particular help elucidate structural interactions and reorientations with the substrate^{8,9} and depict the state of hydration, transition pairwise interaction^{10–12} and electrostatic force^{13–18} as a function of temperature and composition of bioactive molecules.

2. Experimental

Citric acid (AR, BDH) and disodium hydrogen orthophosphate (AR, E Merck) were dried, stored in a P₂O₅ vacuum desiccator and used by weighing out (w/w) for making solutions in deionised, triple-distilled with KMnO₄ and KOH and degassed (by boiling) water of $1 \times 10^{-7} \Omega$ conductance. Densities and flow times were measured with bicapillary pycnometer (of 20 ml volume and 20.22456 g) and low shear Ubbelohde viscometer with 25 ml solution bulb with ± 0.01 K control in temperature at 1 atm pressure. Efflux time was measured with a digital electronic racer with $\pm 1.0 \times 10^{-2} \text{ s}^{-1}$ accuracy. Pycnometer weights were obtained with a ± 0.01 mg Dhona balance model 100 DS and solutions were thermostated for 30 min prior to weighing. Temperature was maintained by circulating cold water from a cooling machine, MK70 GDR, through a thick-walled plastic tube insulated with asbestos thread. A parallel heating assembly with electronic relay encircuited with a thermometer after a 5-watt heating immersion rod were used. Temperature was checked with a calibrated Beckman thermometer (Thermal Division, NPL, New Delhi). The pycnometer was calibrated with aq. NaCl and the viscometer with water.

3. Results and discussion

The r was calculated as

$$r = wt(\text{solution}/wt(\text{solvent})) + 0.0012(1 - wt(\text{solution}/wt(\text{solvent}))).$$

Densities of the solution (r) and solvent (r_0) the buoyancy correction for air (0.0012 (1 - wt (solution/wt(solvent)), molality (m) and weights (wt) were measured with the pycnometer. The error in r is calculated by statistical methods,¹⁹ V_f is computed⁹ from the equation,

$$V_f = 1/r(M - (1000/m)((r - r_0)/(r_0))). \quad (2)$$

M is the molar mass of solute, an uncertainty in V_f is computed from the equation,

$$V_f = (1000/m)\Delta r. \quad (3)$$

$\Delta r = r - r_0$, r_0 is solvent density, viscosity h is calculated from the relation,

$$h = (r \cdot t)/(r_0 \cdot t_0) \cdot h_0. \quad (4)$$

t and t_0 are flow times, h and h_0 are viscosities of solution and solvent respectively. The error in h was obtained like r , the r data are regressed as given below,

$$r = r^0 + S_d m. \quad (5)$$

r^0 is the limiting density at $m \rightarrow 0$, S_d is the slope and V_f values are fitted as,

$$V_f = V_f^0 + S_v m. \quad (6)$$

V_f^0 is the limiting value of V_f . V_f is a measure of the ion-solvent and S_v of the ion-ion interactions. The h values were fitted as $h = h^0 + A_v m$, where h^0 is the limiting viscosity and A_v , the slope. r vs m of DSP in aq. CA and vice versa are plotted in figures 1 and 2, and h of the aq. systems in figure 3. r^0 and h vs m are plotted in figure 4. h^0 vs T , h^0 vs m of aq. CA and DSP, r^0 vs m CA and DSP are shown in figure 5.

4. Binary systems

The r values of 0.050 to 1.25 mol kg⁻¹ aq. NaCl were measured for V_f reproduced to $\pm 0.05/10^{-6}$ m³ mol⁻¹,

which compares well with the literature¹⁸ values. Values of water density^{19a} and viscosity^{19b} were taken from literature: an increase and decrease in r with concentration and temperature respectively, implies formation and breakage of hydrogen bonds. The r^0 values of aq. DSP and CA systems are found higher than that of water by 0.00016, -0.00126, 0.00188, -0.0003 and 0.00021, -0.00024, 0.0015, 0.00014/10 kg m⁻³ at 298.15, 303.15, 308.15 and 313.15 K, respectively (figures 1 and 2). A larger decrease in r^0 of DSP with temperature compared to CA is noted which implies that the ion-solvent interaction of DSP in water compared to CA with water is affected more by thermal energy. Thermal energy seems to weaken electrostatic forces in water. The values indicate slightly stronger molecular interaction of CA than that of DSP and this is, perhaps, due to stronger hydrophilic interaction of undissociated CA with water. The h^0 values of aq. DSP are seen in a range of 0.96422 to 0.59344 from 298.15 to 313.15 K and those of CA from 0.79643 to 0.64677/0.1 kg m⁻¹ s⁻¹. The h^0 of aq. DSP is higher than that of aq. CA by

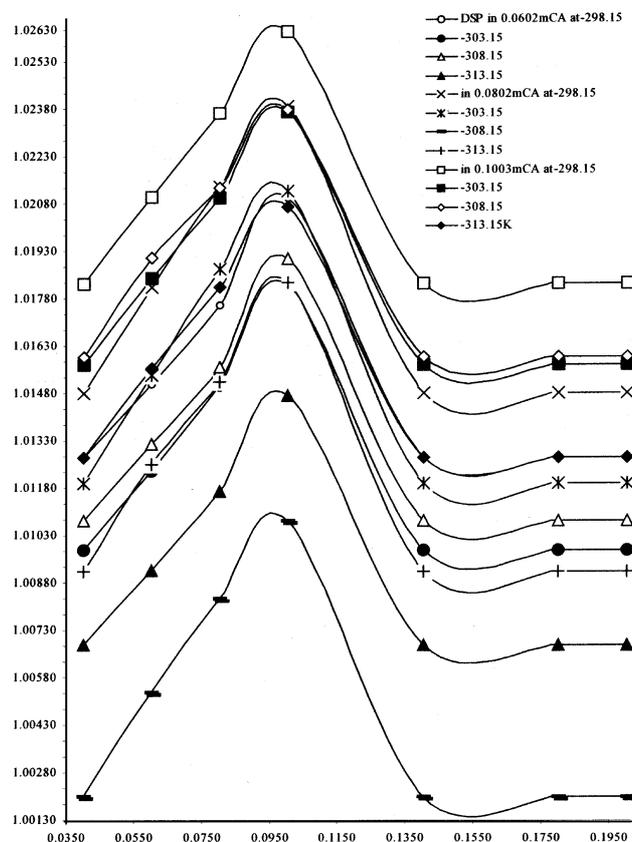


Figure 1. Density vs m of DSP systems in variable compositions of CA at four different temperatures.

0.16779 (figure 3) and the value decrease with temperature. These values denote larger frictional forces on adjacent laminar flow for ion-hydration producing higher values of H^0 . Therefore an ionic solution of DSP could be termed rigid a viscous medium while that of CA a soft medium. A larger decrease in h^0 of DSP than that of CA with temperature seriously destabilizes ion-solvent interactions in DSP-water. The slope constant A_v of h^0 for DSP is found to be between 0.49611 and 0.82629 and that for aq. CA from 2.20745 to 0.17170/0.1 kg m⁻¹ s⁻¹. The V_f^0 values of DSP are obtained in the range 51.37 to 65.46 against those of CA from 101.64 to 106.02/10⁻⁶ m³ mol⁻¹. This indicates that ion-water interactions cause greater internal pressure that seems responsible for contraction in volume while in aq. DSP, CA-water leads to weakening of interaction lowering pressure and producing higher V_f^0 values. For both the systems, V_f^0 values increase with rise in temperature from 298.15 to 303.15 by about 36 and 13.6/10⁻⁶ m³ mol⁻¹ for DSP and CA and in the range 303.15 to 308.15 K, V_f^0 decreases by 54.89 and 17.6/10⁻⁶ m³ mol⁻¹ for DSP and CA respectively. It certifies

that CA introduces an element of thermodynamic stability, due to molecular interactions with water, unlike the ionic DSP. It is important to note that DSP has more effect on transport functions which may be due to ion-ion interaction rather than ion-solvent effects.

5. Ternary system

The r values of DSP in variable composition of CA in water increase from 0.035 to 0.0910 smoothly, then rapidly to 0.1335 mol kg⁻¹ and finally decrease, after 0.1335 to 0.1895 mol kg⁻¹ at a steep slope (figure 1). DSP systems have maximum values at around 0.0910 mol kg⁻¹. Similar pattern of r data for CA in variable composition of DAP in water is noted and depicted in figure 2 with maximum at 0.114 mol kg⁻¹. Notably slopes before and after these compositions are very close and we conclude the same order of composition influence of CA on DSP and vice versa. The higher r values are reported for DSP in 0.1003 m CA at 298.15 and lower values for DSP in 0.0802 m CA at 313.15 K. The maximum r value is noted for 0.095 of CA and 0.114 mol kg⁻¹ of DSP

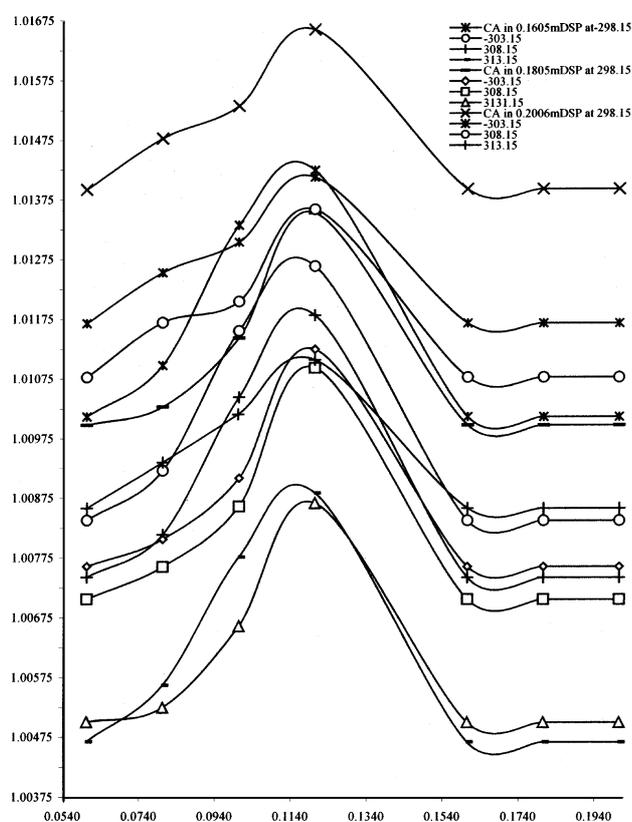


Figure 2. Density vs m of CA in variable compositions of DSP at four temperatures.

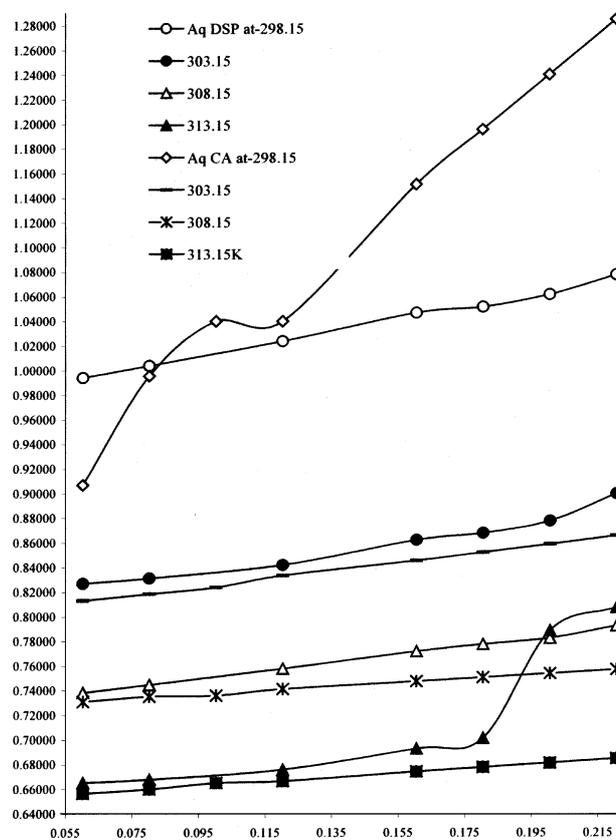


Figure 3. Viscosity vs m of aqueous systems.

(figure 1) and further increase in compositions decrease the r values. However, compositions after 0.1355 of CA and 0.1544 mol kg⁻¹ of DSP have higher r values with slightly lower slopes. At 0.095 and 0.114 mol kg⁻¹ both show bursting of micelles leading to decrease in r but CA and DSP around 0.1355 and 0.1544 mol kg⁻¹ respectively, again lead to micelle formation. This indicates that both mutually balance the behaviour of micelle bursting and thus, can buffer as the best pair for biological studies. For CA in varying concentrations of DSP, a maximum r is seen for CA in 0.2006 m DSP and minimum for 0.1805 m DSP at 298.15 and 313.15 K respectively. The r^0 values of DSP and CA in aqueous solutions have been observed as a linear function of compositions of cosolute (figure 4). Thus densities are higher than that of the binary mixture by 0.00822 at each temperature and larger values for DSP in CA are reported than that for CA in DSP, implying that CA may not break down DSP–water interaction. Na⁺ and HPO₄²⁻ ions may weaken electrostriction of water, which interacts with CA causing weaker CA–water intermolecular forces. Likewise an increase in r^0 values of DSP from aq. to

varying temperatures of aq. CA solution is found as 0.00927, 0.00942, 0.00879, 0.00916/10³ kg m⁻³ at each temperature in 0.0605 m CA and for CA in 0.0605 m DSP as 0.00431, 0.00417, 0.00392 and 0.00415/10³ kg m⁻³. Here, a larger increase is found for DSP in CA while it is lower for CA in DSP with considerable influence of CA on ion–water interactions but DSP has very little influence on molecular interactions of CA with water. The r^0 of DSP in CA with its composition is higher and proves stronger electrostatic forces between CA and water. But r^0 of DSP with varying compositions of CA increase by 0.00307, 0.00312, 0.0029 and 0.00302 at 298.15, 303.15, 308.15 and 313.15 K respectively and for CA with composition of DSP by 0.00142, 0.0038, 0.00130, and 0.00138/10³ kg m⁻³. It implies that CA considerably increases r^0 of DSP while DSP slightly increases the r values of CA. The h^0 values of DSP in aq. CA are higher than that of aq. DSP by 0.03001, 0.02539, 0.01975, 0.04999 and of CA in DSP than that of aq. CA by 0.13352, 0.01986, 0.0094, 0.01042/0.1 kg m⁻¹ s⁻¹. At 298.15 K an increase in h^0 of DSP in 0.0605 to 0.0805 m CA is noted as 0.00993, 0.00982 and 0.04873 and of CA in

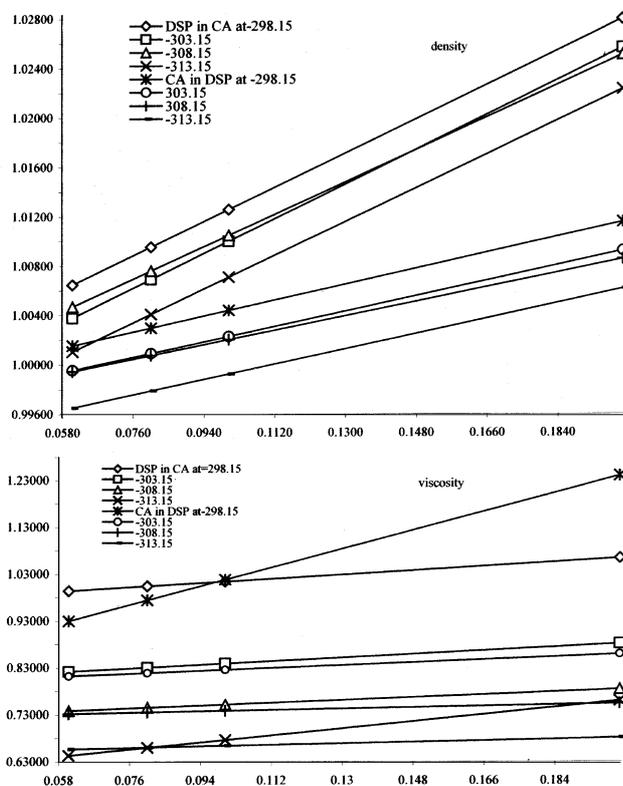


Figure 4. The r^0 vs m of aqueous systems.

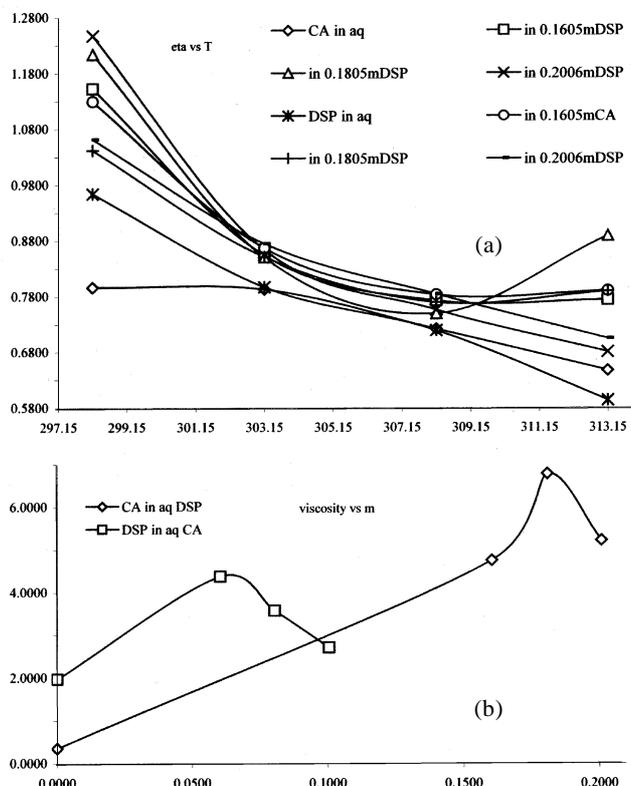


Figure 5. The h^0 vs TK of additive systems. (a) h^0 vs m of additives and (b) r^0 vs m systems.

similar compositions of DSP as 0.04414, 0.04371 and 0.2214/0.1 kg m⁻¹ s⁻¹ and at 303.15, 308.15 and 313.15 K still remain lower. At all DSP compositions, higher h^0 values of CA are found at all temperatures, with maximum effect of composition on CA viscosity. Perhaps the ions Na⁺ and HPO₄²⁻ cause larger frictional forces in the viscous flow of CA solutions than for CA on DSP. An important feature observed in these systems is that micelle formation takes place for lower CA concentrations but higher concentrations of DSP. Interestingly, higher V_f values are found at 303.15 K for both systems separately. Further higher V_f^0 values of CA in aq. DSP prove that ionic interaction of DSP seems to weaken electrostriction of water and intermolecular forces operating between CA and water molecules. The r^0 values of DSP in CA are higher by 0.00513/10 kg m⁻³ but, in general, r^0 of DSP in CA goes down for each composition with temperature. This indicates that molecular interaction of CA enhances electrostriction of water–DSP interaction. The r^0 values of DSP with composition in fixed compositions of CA and CA in DSP are a polynomial relation with compositions of DSP in CA and of CA in DSP. In general, h values are found to be linear for aqueous binary systems as depicted in figure 3, however aq. CA and DSP at 298.15 and 313.15 K induce sharp increase in h at lower and higher concentrations respectively. Figure 3 shows that h value at each temperature is higher for aq. DSP than that for aq. CA indicating stronger interaction in the former. The h values prove that electrostatic forces change in viscous flow and remain less effective. At 298.15, the h^0 value is the lowest for aq. CA and is the highest for CA in 0.2006, 0.1806 and 0.1602 m of DSP. The h^0 values for the binary system converge to a common temperature point. The slope remains constant with respect to temperature. Values of h^0 and r^0 vs m for ternary CA and DSP systems are given in figures 5a and b. The h^0 values of DSP for $m \rightarrow 0$ CA are higher than that of CA for $m \rightarrow 0$ DSP. These values indicate stronger solute–cosolute–solvent interaction for DSP in CA solution compared to CA in DSP solution. However, the h^0 of DSP after 0.055 m CA starts decreasing and continues up to 0.1006 m CA confirming that DSP may be involved in micelle formation at least around 0.055 m CA. Simultaneously the CA for 0 to 0.0157 m DSP increases with almost the same slope values. The h^0 values of CA in DSP and of DSP in CA at 298.15 K are higher than those at other temperatures by

0.02267, 0.17234, 0.18578/0.1 kg m⁻¹ s⁻¹ (figure 5a). These values show that at low temperature the compositions of DSP for CA and of CA for DSP systems cause stronger frictional forces, which resist the flow of an adjacent layer of solution. This effect continues for other compositions as well and may be attributed to cosolute–cosolute interactions. The h^0 values of DSP in 0.0602 m CA are slightly higher than those of CA for 0.1605 m DSP at 298.15 K which confirms that molecular interactions of CA enhance the frictional force of DSP–water interactions more than that of DSP in CA–water. The h^0 values are regressed against temperature and coefficients are referred to h_T^0 , the limiting viscosity and A_T , slope constants at temperature approaching 0 value. The h_T^0 of aq. DSP is higher than that of aq. CA by 1.6244. The h_T^0 of CA in aq. DSP are higher by 0.37759, 3.2115 and 2.50658/0.1 kg m⁻¹ s⁻¹ at 0.1605, 1.805 and 0.2005 m DSP. On transferring DSP to aq. CA, the h^0 drastically decreases to lower values than those of CA in aq. DSP. It implies that CA disrupts frictional forces of aq. DSP and this action dominates for 0.0605 m CA but at higher concentrations of CA, it decreases. Similar trends are also observed for CA with compositions of DSP. The A_T values are negative and of DSP in CA is higher than that of CA in aq. DSP, which proves that thermal energy decreases the frictional force. We note that higher compositions of CA result in lower V_f^0 values probably due to predominance of CA–CA and CA–DSP interactions over CA–water and DSP–water interactions.

6. Conclusion

The r^0 values of aq. DSP decrease more with temperature compared to CA, perhaps, due to weakening of electrostatic forces of hydrated Na⁺ and HPO₄²⁻. Maximum value of r of DSP in 0.0910 mol kg⁻¹ CA solution in water and 0.114 mol kg⁻¹ DSP with positive and negative slopes before and after these compositions denote bursting and reorganization of micelles respectively. Higher densities for ternary systems than those for binary, with larger values for DSP in aqueous solutions of CA than that of CA in aqueous solution of DSP show CA weakens electrostriction of water. Higher r^0 for DSP in CA solution shows stronger electrostatic forces between CA and water. The higher h^0 of DSP in aq. CA than that in water alone of CA in aq. DSP than that of CA in water implies larger frictional forces in viscous flows of

CA and DSP solutions due to the presence of Na^+ and HPO_4^{2-} . The lower V_f of aq. DSP compared to that of aq. CA proves greater internal pressure for ionic interactions in DSP solution. The V_f^0 values converge to a particular composition due to micelle formation and higher V_f^0 values of CA in aq. DSP prove weakening of water and CA–water electrostrictions. The higher h values of aq. DSP compared to that of aq. CA is attributed to electrostatic forces on flow, converging h^0 values of the binary system to a fixed temperature. The higher h^0 values of DSP for $m \rightarrow 0$ CA compared to that of CA for $m \rightarrow 0$ DSP, depict stronger solute–cosolute–solvent interaction for DSP in CA than that of CA in DSP.

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