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Solubility and the solution thermodynamics of l-proline in the aqueous binary mixture of NaCl and KCl solution

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ABSTRACT

This paper presents a comprehensive investigation into the equilibrium solubility and thermodynamic behavior of l-proline, a biologically and pharmaceutically significant protogenic non-essential amino acid, in both aqueous and aqua-electrolytic solutions. The study explores the effects of concentration variations at specific temperatures and temperature variations at specific concentrations. The experimental analysis is conducted using analytical gravimetric techniques. The observed phenomena are explained based on various chemical interactions, including ion-dipole and dipole-dipole interactions, present in electrolytic and pure aqueous solutions of the amino acid. The salting in/out effect is also considered to support the solubility results. The experimental results demonstrate that l-proline exhibits increased solubility in the presence of electrolytes compared to pure aqueous solutions, considering the variations in both temperature and concentration. Furthermore, the solubility of l-proline is found to be higher in the presence of KCl than NaCl as an electrolyte in aqueous media. The physical properties and sizes of both the amino acid and electrolytes are identified as crucial factors influencing the observed solubility trends.

1. Introduction

The human body operates as a complex solvent system, encompassing an assortment of biological fluids responsible for dissolving and facilitating essential bodily functions. The amino acids play a crucial to build a block of protein chain and takes part on biological metabolism [1]. Thus, their solubility and solvation thermodynamics is one of the important factors to study the complex mechanism in living organism. It has in impact on industrial application such as metal extraction [2], cosmetic production [3] and drug delivery for human body organ [4]. Studying the solubility and solvation thermodynamics of amino acids in binary solvents could aid in the investigation of how ions and small molecules interact with bio-macromolecules. The conformational changes and the nature of proteins like macromolecules in solution in the presence of electrolytes can be frequently investigated by thermodynamic characteristics [3,5–7]. The physicochemical behaviour of amino acids is strongly influenced by the dielectric constant of the binary or ternary solvent mixtures in which they are immersed as well as by electrostatic interactions. The solvation nature of amino acids in a specific solvent system is also affected by hydrophobicity / hydrophilicity and polarizability [8]. Therefore, a profound understanding of solvation chemistry is necessary for analyzing the relevant amino acid in a complex system. It is important to note that free amino acid molecules are not commonly found in nature and are typically generated through the fermentation process or by hydrolysing materials that contain proteins [9]. These techniques are highly dependent on a variety of inorganic salts at different concentrations as well as understanding of salts effect on the solubility of amino acids at various temperatures. Based on

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the interesting application, a number of solubilities results in the literature already have reported for amino acids in pure aqueous [9–12], aqueous-organic [13–16], non-aqueous [17–19], and aqueous-electrolyte mixtures [20–25]. Thus, newly addition of unreported data will undoubtedly enhance the effectiveness in this research field. Several reports show the influence of electrolyte on amino acids structure as well as physical and chemical properties based on several weak interactions in binary mixture of solution [17,26]. Held and co-workers disclosed the specifics and characteristics of ternary electrolyte-amino acid–water solutions system [26].

Building on prior research, our goal was to investigate the solubility of l-proline in aqueous binary mixtures containing NaCl and KCl. We aimed to understand its solubility behavior and propose a solvation mechanism. The study comprehensively analyzed l-proline's saturation solubility and thermodynamic properties across five different temperatures in solutions with varying concentrations of NaCl and KCl. To elucidate l-proline's solvation thermodynamics and stability, we employed theoretical approaches that considered various weak interactions.

2. Experimental section

2.1. Chemicals and purification

The l-proline used in the experiments was procured from SRL with a purity of 99.0 % and its melting point is 501 K. Upon purchase, the l-proline was subjected to a drying process in a desiccator at 350 K for duration of 5 days. The electrolytes, NaCl and KCl, were obtained from Merck, India. Prior to their use, these salts were dried in an oven at 400 K for 4 days and subsequently cooled in a vacuum desiccator for 7 days to prevent moisture absorption. Throughout the entire study, the experimental solutions were prepared using triple distilled water. Table 1 provides detailed information regarding the chemicals utilized in the study.

2.2. Experimental procedure

The experimental procedure employed in this study involved the use of analytical gravimetry, which encompassed several stages. The solubility of l-proline was investigated under two conditions: at a constant temperature and over a range of temperatures (288.15 K to 308.15 K) at least three times for each experimental condition. Temperature control was achieved using a thermostat with an accuracy of ± 0.10 K at atmospheric pressure. At a specific temperature (298.15 K), saturated solutions of l-proline were prepared separately in aqueous NaCl and aqueous KCl, with different concentrations as indicated in the molality column of Table 2. To establish equilibrium, these solutions were continuously stirred for 24 h. Subsequently, the stirred solutions were allowed to settle undisturbed for 7 h prior to sampling, ensuring that any undissolved amino acids had settled down. In gravimetric estimation, maintaining the saturation of solutions while transitioning between higher and lower temperatures presents challenges. This difficulty arises because the temperature-dependent solubility of a solid, such as amino acid l-proline, in solvent mixtures impacts the process. The solubility of l-proline in the solution increases as temperature rises. When the temperature of a saturated solution increases, it becomes unsaturated, while decreasing the temperature leads to supersaturation. To address this issue, in current experiments employed various solution sets at different temperatures to achieve saturation of l-proline solutions, mitigating these challenges. A volume of 5 mL from the supernatant liquid was extracted using pre-dried pipettes and transferred into glass vessels. The extracted solutions were then filtered using 0.22 μm HPLC disposable filters and promptly weighed. Subsequently, the solvent (water) was completely removed slowly through evaporation using a hot air oven. This resulted in an increase in the crystalized amount of the amino acid. For complete drying of the crystallized solute a drying stove was set at a temperature of 410.15 K.

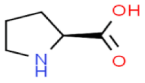
All the dried samples are cooled in a dehydrator containing silica gel for 48 hrs and weighed. The process used in the entire study was doing with regular interval until reached a constant weight. The maximum variation during estimation were noticed as = 0.004 mol·kg^{-1}, leading to the conclusion that any significant amount of electrolyte was neither precipitated nor adsorbed on the solid amino acid. In other word we can

Table 2
Solubility [the mean of three experiments (±standard deviation)] of l-proline (mol·kg^{-1}) of water) in pure water and water + NaCl & H_2O + KCl in different composition of NaCl & KCl at different temperatures (K)[#] under atmospheric pressure, p = 0.1 MPa[a].

NaCl (mol·kg^{-1})	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
0.00	13.80 ± 0.08	14.58 ± 0.09	15.30 ± 0.11	16.04 ± 0.14	16.87 ± 0.08
0.25	13.85 ± 0.11	14.65 ± 0.10	15.41 ± 0.10	16.15 ± 0.08	16.98 ± 0.07
0.50	13.98 ± 0.08	14.76 ± 0.07	15.54 ± 0.06	16.29 ± 0.06	17.10 ± 0.15
1.00	14.12 ± 0.14	14.94 ± 0.11	15.70 ± 0.05	16.44 ± 0.11	17.28 ± 0.13
1.25	14.23 ± 0.14	15.02 ± 0.08	15.79 ± 0.14	16.56 ± 0.09	17.38 ± 0.12
1.50	14.32 ± 0.10	15.12 ± 0.06	15.88 ± 0.13	16.72 ± 0.11	17.46 ± 0.08
KCl (mol·kg^{-1})					
0.00	13.80 ± 0.08	14.58 ± 0.09	15.30 ± 0.11	16.04 ± 0.14	16.87 ± 0.08
0.25	13.96 ± 0.11	14.70 ± 0.06	15.46 ± 0.08	16.26 ± 0.11	17.06 ± 0.10
0.50	14.11 ± 0.07	14.88 ± 0.09	15.67 ± 0.06	16.44 ± 0.10	17.22 ± 0.12
1.00	14.44 ± 0.13	15.18 ± 0.14	15.96 ± 0.09	16.74 ± 0.08	17.54 ± 0.10
1.25	14.62 ± 0.08	15.34 ± 0.09	16.10 ± 0.12	16.90 ± 0.14	17.66 ± 0.11
1.50	14.86 ± 0.14	15.54 ± 0.09	16.28 ± 0.06	17.08 ± 0.04	17.80 ± 0.09

Uncertainties in temperature u(T)[#] = 0.10 K; Relative uncertainties in pressure $u_r(p)$ [a] = 0.01 MPa.

Table 1
Specification of chemical samples.

Chemical name	Chemical structure	Source	CAS Registry No.	Initial purity[a] (fraction)	Drying method & Purification of chemicals	Final purity
l-proline		SRL, India	7447–40-7	99.0 %	drying in a dehydrator with silica gel	99.5 %
Sodium chloride	NaCl	E. Merck, Bombay, India	7647–14-5	98.5 %	Oven dried	98.5 %
Potassium chloride	KCl	E. Merck, Bombay, India	147–85-3	98.5 %	Oven dried	98.5 %
Water	H_2O	Distilled water	DE2DF72721		distillation	–

[a] Declared by supplier.

Table 3
Relative solubility l-proline in water and water + NaCl & H_2O + KCl in different composition of NaCl and KCl at different temperatures.

Salt Conc^n	288.15 K		293.15 K		298.15 K		303.15 K		308.15 K	
NaCl (mol·kg^{-1})	Relative Solubility (S_S/S_R)	Log (S_S/S_R)	Relative Solubility (S_S/S_R)	Log (S_S/S_R)	Relative Solubility (S_S/S_R)	Log (S_S/S_R)	Relative Solubility (S_S/S_R)	Log (S_S/S_R)	Relative Solubility (S_S/S_R)	Log (S_S/S_R)
0.25	1.004	0.0017	1.005	0.0022	1.007	0.0030	1.007	0.0030	1.007	0.0030
0.50	1.013	0.0056	1.012	0.0052	1.016	0.0069	1.016	0.0069	1.013	0.0056
1.00	1.023	0.0098	1.025	0.0107	1.026	0.0111	1.025	0.0107	1.024	0.0103
1.25	1.031	0.0133	1.030	0.0128	1.032	0.0137	1.032	0.0137	1.030	0.0128
1.50	1.038	0.0162	1.037	0.0158	1.038	0.0162	1.042	0.0179	1.035	0.0149
KCl (mol·kg^{-1})	288.15 K		293.15 K		298.15 K		303.15 K		308.15 K	
0.25	1.012	0.0052	1.008	0.0035	1.010	0.0043	1.014	0.0030	1.011	0.0030
0.50	1.022	0.0095	1.021	0.0043	1.024	0.0103	1.025	0.0069	1.021	0.0056
1.00	1.046	0.0195	1.041	0.0175	1.043	0.0183	1.044	0.0107	1.040	0.0103
1.25	1.059	0.0249	1.052	0.0220	1.052	0.0220	1.054	0.0137	1.047	0.0128
1.50	1.077	0.0322	1.066	0.0278	1.064	0.0269	1.065	0.0179	1.055	0.0149

conclude that isolated solid material is only the crystal of l-proline. To calculate the amount of amino acid present in the mixture, first we measure the weight of the empty glass vessel, secondly, glass vessel with amino acid solution taken via. 0.22 μm HPLC disposable filter and then the weight of glass vessel with well dried sample. If the weight of glass vessel with solution taken as W_1 g and the glass vessel after complete evaporation of water is as W_2 g, then the amount of evaporated water would be, $W = (W_1 - W_2)$ g then the weight of amino acid dissolved in W g of water would be $(W_2 - W_3 - W_4)$ where W_3 g and W_4 g are the weight of empty glass vessel and the minimum amount of electrolyte present in evaporated water. From this we measured the solubility of l-proline in g per kg of water as: $S_1 = (W_2 - W_3 - W_4) / (W) \times 1000$ g $= (W_2 - W_3 - W_4) / (W_1\text{-}W_2) \times 1000$ g. And the solubility in mole per kg of solvent would be suppose $S = S_1/M$ where M = molecular weight of l-proline. From the mole per kg of water one can easily calculate the mole fraction solubility of l-proline in water. The following equation was used to measure the mole fraction solubility of l-proline (X_1) and the mole fraction solubilities are also shown in Supplementary Information section in Table S1.

$$X_1 = (m_1/M_1)/(m_1/M_1 + m_2/M_2 + m_3/M_3)$$

Here m_1, m_2 and m_3 denote the mass of l-proline, electrolyte and water respectively while M_1, M_2, M_3 represent the molecular mass of l-proline, electrolyte, and water respectively. Similar process was done while electrolytic mixture having different concentration.

Previous studies have demonstrated that this gravimetric approach does not result in any significant adsorption or precipitation of electrolyte onto l-proline.

Another important study (PXRD) to justify the solid-phase only pure amino acid was performed. To obtain PXRD patterns for the raw materials and residual solids, have conducted X-ray powder diffraction analysis on the recrystallized samples of l-proline obtained from aqueous NaCl and KCl solutions. The results demonstrate a strong agreement between the diffraction patterns of these recrystallized samples and those of pure l-proline. Notably, there are slight differences in the PXRD patterns of l-proline when it is in electrolyte solutions compared to its pure form. These variations in peak intensities can be attributed to either the molecular rearrangements within the crystal lattice during the recrystallization process or the dynamic equilibrium between the residual solid or the solution.

However, it is important to emphasize that the overall crystal phase remains unchanged throughout the experiment, indicating the preservation of l-proline's chemical integrity and crystal structure. Furthermore, the examination of the solubility of the residual solid phase of l-proline reveals no significant alterations when compared to pure l-proline.

To see the major interaction of l-proline in the aqueous electrolyte solutions also performed the UV–Vis studies. The UV–Visible spectra were recorded in a Shimadzu UV 1900 UV Visible spectrophotometer using quartz cuvette of 1 cm path length. The baseline was set in pure water. Detail is discussed in solubility discussion section.

3. Theoretical

3.1. Theoretical study of total transfer Gibbs free energy and entropy of solution

The following equation was used to calculate the Gibbs energy of l-proline solution on molal scale at the used studied temperatures [27,28] and the data shown in Table 4.

$$\Delta G_s^0(i) = -RT\ln S\gamma \approx -RT\ln S \quad (1)$$

In this study, the amino acids are regarded as zwitterions in solutions and the activity coefficient and solubility in molal scale are γ and S respectively. This zwitterions formation leads to large dipole–dipole interaction thus activity coefficient is an important factor here. In the previous study, several methods were applied to solve the complexity of activity coefficients and consider unity for easy calculations [29–32]. Here, the activity coefficient is considered to be unity to calculate the total transfer free energy [$\Delta G_t^0(i)$] for the investigated water-NaCl/KCl electrolytic solutions. In the present research, the primary focus revolves around the transfer Gibbs free energy, aiming to relate it to solubility outcomes and elucidate the dissolution mechanism of amino acids. While assessing the Gibbs free energy of solution ($\Delta G_s^0(i)$), we assume a constant activity coefficient (γ) equal to one for this study. The main focus of the study is on determining the standard total transfer Gibbs energies ($\Delta G_t^0(i)$) for l-proline in experimental chloride aqueous solutions. The calculation of $\Delta G_t^0(i)$ involves factors associated with activity coefficients, but in this study, we consider them negligible. Therefore, the assumption of ignoring the impact of activity coefficients on the estimation of $\Delta G_t^0(i)$ appears reasonable.

Since, $\Delta G_t^0(i)$ is associated as: $\Delta G_t^0(i) = \Delta G_s^0(i) - \Delta G_R^0(i)$ (Where $\Delta G_s^0(i)$ and $\Delta G_R^0(i)$ are the free energy of the l-proline of NaCl/KCl solvent and water respectively), so, $\Delta G_t^0(i) - RT\ln m_s\gamma_s + RT\ln m_R\gamma_R = -RT\ln m_s\gamma_s/\ln m_R\gamma_R = -RT\ln m_s/m_R = -RT\ln(m_s\gamma_s) + RT\ln(m_R\gamma_R) = -RT\ln(m_s\gamma_s/m_R\gamma_R) = -RT\ln(m_s/m_R) - RT\ln(\gamma_s/\gamma_R)$ Hence the activity coefficient factor, $-RT\ln\gamma_s/\gamma_R$ ('s' stands for aqueous NaCl and KCl, whereas 'R' for H_2O), which tends to be negligibly small. Thus, the assumption of ignoring the impact or contribution of activity coefficient in the present study for the estimation of total transfer Gibbs free energy may be reasonable. Further $\Delta G_s^0(i)$ (Table 4) are fitted by the least square method at obtained different temperatures to calculated a, b and c coefficients (Eq. (2) (Table 5)[13,28].

Table 4
Gibbs free energy ($kJ{\cdot}mol^{-1}$) at different respective solubilities of l-proline at different temperature in chloro-aqueous media of sodium and potassium respectively.

288.15 K		293.15 K		NaCl + water 298.15 K		303.15 K		308.15 K	
S ($mol{\cdot}kg^{-1}$)	ΔG^0_{sol} (i) ($kJ{\cdot}mol^{-1}$)	S ($mol{\cdot}kg^{-1}$)	ΔG^0_{sol} (i) ($kJ{\cdot}mol^{-1}$)	S ($mol{\cdot}kg^{-1}$)	ΔG^0_{sol} (i) ($kJ{\cdot}mol^{-1}$)	S ($mol{\cdot}kg^{-1}$)	ΔG^0_{sol} (i) ($kJ{\cdot}mol^{-1}$)	S ($mol{\cdot}kg^{-1}$)	ΔG^0_{sol} (i) ($kJ{\cdot}mol^{-1}$)
13.8	−6.2879	14.58	−6.5310	15.3	−6.7619	16.04	−6.9943	16.87	−7.2389
13.85	−6.2965	14.65	−6.5427	15.41	−6.7796	16.15	−7.0115	16.98	−7.2556
13.98	−6.3189	14.76	−6.5609	15.54	−6.8005	16.29	−7.0333	17.10	−7.2736
14.12	−6.3428	14.94	−6.5904	15.7	−6.8258	16.44	−7.0564	17.28	−7.3004
14.23	−6.3614	15.02	−6.6035	15.79	−6.8400	16.56	−7.0747	17.38	−7.3152
14.32	−6.3765	15.12	−6.6196	15.88	−6.8541	16.72	−7.0989	17.46	−7.3270
				KCl + water					
288.15 K		293.15 K		298.15 K		303.15 K		308.15 K	
S ($mol{\cdot}kg^{-1}$)	ΔG^0_{sol} (i) ($kJ{\cdot}mol^{-1}$)	S ($mol{\cdot}kg^{-1}$)	ΔG^0_{sol} (i) ($kJ{\cdot}mol^{-1}$)	S ($mol{\cdot}kg^{-1}$)	ΔG^0_{sol} (i) ($kJ{\cdot}mol^{-1}$)	S ($mol{\cdot}kg^{-1}$)	ΔG^0_{sol} (i) ($kJ{\cdot}mol^{-1}$)	S ($mol{\cdot}kg^{-1}$)	ΔG^0_{sol} (i) ($kJ{\cdot}mol^{-1}$)
13.8	−6.2879	14.58	−6.5310	15.3	−6.7619	16.04	−6.9943	16.87	−7.2389
13.96	−6.3155	14.7	−6.5510	15.46	−6.7876	16.26	−7.0286	17.06	−7.2676
14.11	−6.3411	14.88	−6.5806	15.67	−6.8211	16.44	−7.0564	17.22	−7.2915
14.44	−6.3965	15.18	−6.6293	15.96	−6.8665	16.74	−7.1020	17.54	−7.3387
14.62	−6.4261	15.34	−6.6548	16.1	−6.8882	16.9	−7.1259	17.66	−7.3562
14.86	−6.4652	15.54	−6.6864	16.28	−6.9158	17.08	−7.1526	17.8	−7.3764

Table 5
Coefficients a, b and c, Gibbs energies $\Delta G^0_t(i)$, and entropies $T\Delta S^0_t(i)$ of transfer l-proline in chloro-aqueous solution of Na and K respectively in different electrolytic composition at 298.15 K.

NaCl ($mol{\cdot}kg^{-1}$)	a ($kJ{\cdot}mol^{-1}$)	b ($kJ{\cdot}mol^{-1}{\bullet}K^{-1}$)	c ($kJ{\cdot}mol^{-1}{\bullet}K^{-1}$)	$\Delta G^0_t(i)$ ($kJ{\cdot}mol^{-1}$)	$T\Delta S^0_t(i)$($kJ{\cdot}mol^{-1}$)
0.00	5.06	0.0040	−0.00767	0.0000	0.0000
0.25	12.13	−0.1527	0.01567	−0.0237	0.0878
0.50	12.58	−0.1640	0.01738	−0.0654	0.0181
1.00	13.47	−0.1846	0.02044	−0.1678	0.0020
1.25	9.88	−0.1046	0.00852	−0.1759	−0.0700
1.50	17.34	−0.2724	0.03356	−0.2302	−0.0652
KCl ($mol{\cdot}kg^{-1}$)					
0.00	5.06	0.0040	−0.00767	0.0000	0.0000
0.25	−14.87	0.4494	−0.07411	−0.0329	−0.1575
0.50	14.46	−0.2073	0.02385	−0.0989	−0.1131
1.00	4.09	0.0225	−0.01039	−0.2088	−0.2182
1.25	3.20	0.0390	−0.01278	−0.2708	−0.3966
1.50	0.33	0.0980	−0.02147	−0.3431	−0.6656

Relative error of $\Delta G^0_t(i)$ and $T\Delta S^0_t(i)$ lies in the range of ± (0.2 to 1.5) %.

$$\Delta G^0_s(i) = a + bT + cTlnT \tag{2}$$

$\Delta G^0_t(i)$ and ΔS^0_t of the l-proline at aqueous NaCl/KCl solutions were estimated by using equation (3) and (4) at 298.15 K [13,28].

$$\Delta G^0_t(i)\Delta G^0_t(i)\Delta G^0_t(i) = \Delta G^0_s(i) - \Delta G^0_R(i)$$

$$\Delta G^0_t(i) = (a_s - a_R) + (b_s - b_R)T + (c_s - c_R)T\ln T - RT\ln(M_s/M_R) \tag{3}$$

$$\Delta S^0_t(i) = (b_R - b_s) + (c_R - c_S)(1 + \ln T) + R\ln(M_s/M_R) \tag{4}$$

'R' for reference solvent (water) and 's' for cosolvent (electrolyte solution).

M_R and M_s are the molar mass of the used pure water and aqueous NaCl/KCl solution respectively. The evaluated data of $\Delta G^0_t(i)$ and T $\Delta S^0_t(i)$ are shown in Table 6.

3.2. Calculation of transfer energetics

The total transfer energetics is expressed as below in the form of equation was described in detail earlier [17,27] and the evaluated data are summarized in Table 6.

$$\Delta P^0_t(i) = \Delta P^0_{t,cav}(i) + \Delta P^0_{t,d-d}(i) + \Delta P^0_{t,ch}(i) \tag{5}$$

Further, the $\Delta P^0_{t,cav}(i)$ values were calculated using scale particle theory (SPT) [19,32] by considering the amino acids and NaCl/KCl molecules as hard sphere and the equations are given below [33–35].

$$\Delta G^0_{t,d-d}(i) = ({}_s\Delta G^0_{d-d}(i) - {}_R\Delta G^0_{d-d}(i) \tag{6}$$

and $\Delta S^0_{t,d-d}(i) = ({}_s\Delta S^0_{d-d}(i) - {}_R\Delta S^0_{d-d}(i))$

$${}_s\Delta G^0_{d-d}(i)(8\Pi/9)N^2_A\mu^2_s\mu^2_x\sigma^{-3}_{s-x}(kT)^{-1}V^{-1}_s = A/T\,V_s \tag{7}$$

Where, A = $-(8\Pi/9)N^2_A\mu^2_s\mu^2_x\sigma^{-3}_{s-x}(k)^{-1}$ and $V_s = M_s/d_s$.
and that of $\Delta S^0_{d-d}(i)$ as follows—

$$-{}_s\Delta S^0_{d-d}(i) = -\{\delta\,{}_s\Delta G^0_{d-d}(i)/\delta T\}_p \tag{8}$$

i.e.,$T\,{}_s\Delta S^0_{d-d}(i) = {}_s\Delta G^0_{d-d}(i)[1 + T\alpha]$, N is Avogadro's number, μ_s, μ_x are the dipole moment (Table S2) of aqueous NaCl/KCl solution and l-proline respectively.$\sigma_{s-x} = 1/2(\sigma_s + \sigma_x)$ where σ_s and $\sigma_x$are the hard sphere diameter of aqueous NaCl/KCl solution and l-proline molecule respectively (Table S2) [32,36].

$$\alpha = (\delta\ln V_s/\delta T)_P = -(\delta\ln d_s/\delta T)_P \tag{9}$$

Again, actual mole fraction can be obtained by multiply of X_{S1} by mole fraction of dipole–dipole interaction $\Delta P^0_{t,d-d}(i)$ [34,37]

Table 6
Gibbs energies of transfer $\Delta G_t^0(i)$,$\Delta G_{t,cav}^0(i)$,$\Delta G_{t,d-d}^0(i)$,$\Delta G_{t,ch}^0(i)$ and enthalpy, $\Delta H_{t,cav}^0(i)$ and entropies of transfer $T\Delta S_t^0(i)$,$T\Delta S_{t,cav}^0(i)$, $T\Delta S_{t,d-d}^0(i)$ and $T\Delta S_{t,ch}^0(i)$ of l-proline in different composition of chloro-aqueous solution of alkali metals (Na & K) at 298.15 K in kJ·mol^{-1}.

Molality (mol·kg^{-1})	$\Delta G_t^0(i)$(kJ·mol^{-1})	$\Delta G_{t,cav}^0(i)$(kJ·mol^{-1})	$\Delta G_{t,d-d}^0(i)$ (kJ·mol^{-1})	$\Delta G_{t,ch}^0(i)$(kJ·mol^{-1})	$T\Delta S_t^0(i)$(kJ·mol^{-1})	$\Delta H_{t,cav}^0(i)$(kJ·mol^{-1})	$T\Delta S_{t,cav}^0(i)$(kJ·mol^{-1})	$T\Delta S_{t,d-d}^0(i)$(kJ·mol^{-1})	$T\Delta S_{t,ch}^0(i)$(kJ·mol^{-1})
l-proline in NaCl + H_2O									
0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.25	−0.0237	−0.0358	−0.0038	0.0159	0.0878	−0.0026	0.0332	−0.0041	0.0587
0.50	−0.0654	−0.0693	−0.0151	0.0190	0.0181	−0.0050	0.0643	−0.0163	−0.0299
1.00	−0.1678	−0.1360	−0.0629	0.0311	0.0020	−0.0098	0.1262	−0.0677	−0.0565
1.25	−0.1759	−0.1677	−0.0993	0.0911	−0.0700	−0.0120	0.1557	−0.1069	−0.1188
1.50	−0.2302	−0.1989	−0.1451	0.1138	−0.0652	−0.0142	0.1847	−0.1562	−0.0937
l-proline in KCl + H_2O									
0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.25	−0.0329	−0.0710	−0.0039	0.0420	−0.1575	−0.0051	0.0659	−0.0042	−0.2192
0.50	−0.0989	−0.1370	−0.0182	0.0563	−0.1131	−0.0047	0.0623	−0.0196	−0.1558
1.00	−0.2088	−0.2687	−0.0646	0.1245	−0.2182	−0.0187	0.2500	−0.0695	−0.3987
1.25	−0.2708	−0.3305	−0.1017	0.1614	−0.3966	−0.0228	0.3077	−0.1095	−0.5948
1.50	−0.3431	−0.3902	−0.1483	0.1954	−0.6656	−0.0266	0.3636	−0.1596	−0.8696

$$X_{s1} = X_s(\mu_s/\sigma_s^3)/(\mu_R/\sigma_R^3) \tag{10}$$

After subtraction of $\Delta P_{t,cav}^0(i)$ and $\Delta P_{t,d-d}^0(i)$ from the $\Delta P_t^0(i)$, we get the value of $\Delta P_{t,ch}^0(i)$ which are presented in Table 6.

4. Discussion

4.1. Solubility and relative solubility

The solubility of l-proline is measured the in five different molal concentrations of potassium and sodium salts in water at different temperatures and results were compared with the earlier literature [38,39] in pure water that excellently justified the measurement in the present method. The results showed in Table S2 in supplementary Information.

The data analysis shows the variation of solubility as well as relative solubility of l-proline from various corners viz.

(a). The solubility of l-proline increases with an elevation in temperature in the absence of electrolyte.

(b). The solubility of l-proline also shows an increase with higher electrolytic concentrations at a specific temperature, as depicted in Fig. 2 and Fig. 3.

c). Amino acid l-proline exhibits greater solubility in KCl compared to NaCl at specific concentrations and temperatures, as shown in Figs. 4 and 5.

d). At a particular electrolytic concentration, the solubility of l-proline grows up with an increasing temperature, as illustrated in Figs. 6 and 7.

In l-proline there basically exist ion-ion interactions in solution because of its zwitterionic form. First, observation may be the result of the increased kinetic energy of water molecules with temperature hike. This aids the solvent molecule in deforming the l-proline molecule association bound together by strong intermolecular force. As a result, l-proline may now interact with solvent molecules effectively, increasing solubility.

To support the solubility and the absent of any chemical reaction was studied based on UV–vis spectroscopy of individual solute, electrolytes and both in the aqueous solutions. The absorption of individual chemical and their mixture in the solution did not show any appearance of an extra peak proves the absent of chemical reactions (Fig. 8). An interaction between biomolecule and the electrolyte become the sole parameter during the consideration of solubility of l-proline in that electrolyte and this is the pillar on which we can explain the second observation. When l-proline ($^+A^-$) dissolve in aqueous solution of NaCl/KCl(B^+C^-) the following reaction takes place:

$$(^+A^-) + (B^+C^-) \langle\!\!-\!\!\rangle\ B^+(^-A^+)\ C^-(11)$$

The obtained ion-pair complex shield hydrophobic part of the amino acid l-proline and consequently the hydrophilic part become more expose for making interaction with solvent water molecules resulting enhancement of the solubility of l-proline in present of NaCl/KCl in the solution. Positive value of salting-in constant also supports this observation.

Here the present Cl^- as negative ions in the solution is responsible for the salting in effect. Greater the value of salting in constant [Table 7] higher will be the solubility. This fact co-relates relative solubilities values as shown in Table 3 and Figs. 4 & 5. The K_{si} (constant for salting-in/out actually known as Setchenow constant) at 298.15 K, is a quantitative measurement was determined using Eq. (12) [40] as below.

$$\log(S/S_W) = K_{si}/C \tag{12}$$

Here S and Sw are the solubility of the studied l-proline in aqueous NaCl/KCl solutions and pure water respectively with C concentration in molality at 298.15 K. The evaluated corresponding values are shown in

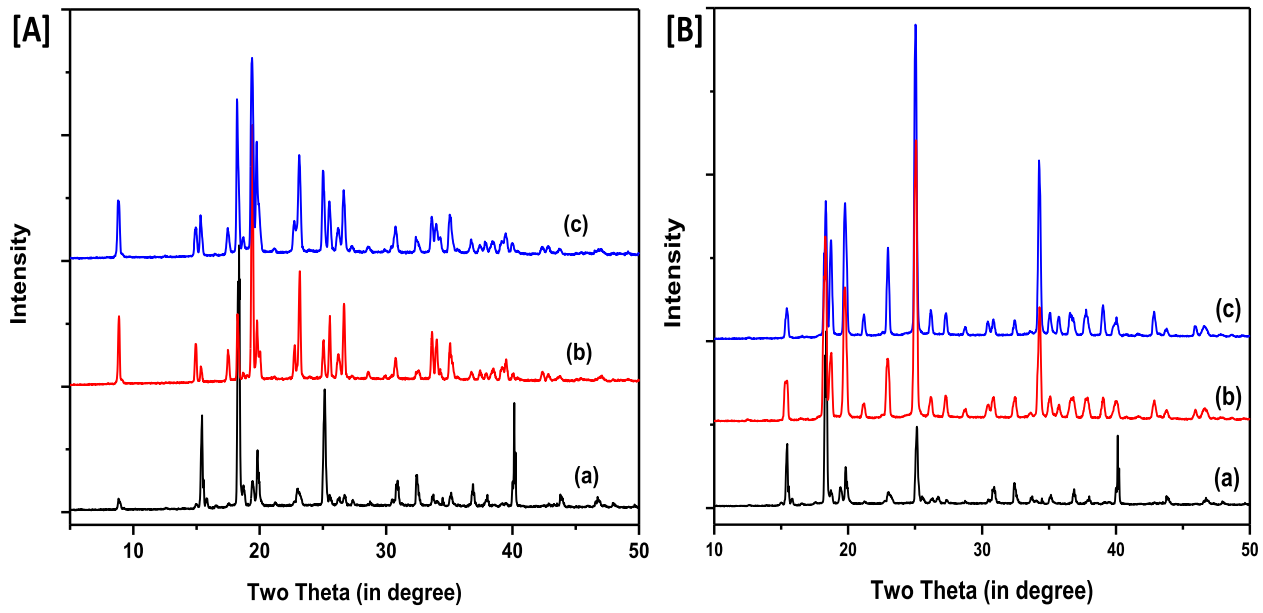


Fig. 1. Comparison of X-ray powder diffraction patterns of (a) pure l- proline and (b) residual solid-phase l-proline from aqueous NaCl solution (c) residual solid-phase l-proline from aqueous KCl solution; [B] Comparison of X-ray powder diffraction patterns of (a) pure l- proline and (b) recrystalized solid-phase l-proline from aqueous NaCl solution (c) recrystalized solid-phase l-proline from aqueous KCl solution.

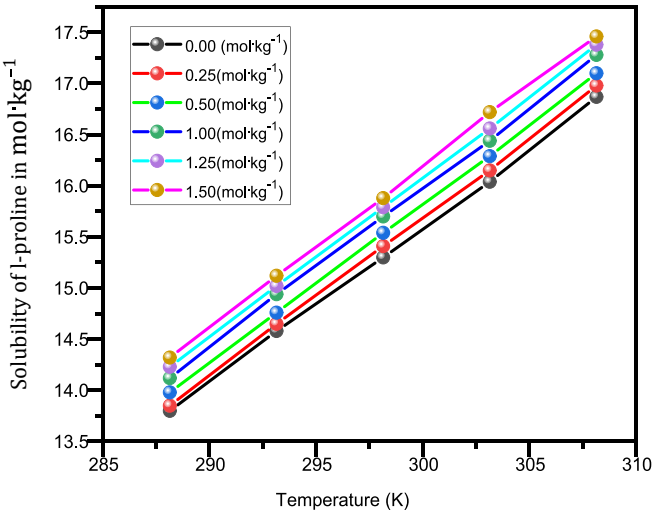


Fig. 2. Solubility fluctuation of l-proline in NaCl-water at different concentration by keeping constant temperature (298.15 K).

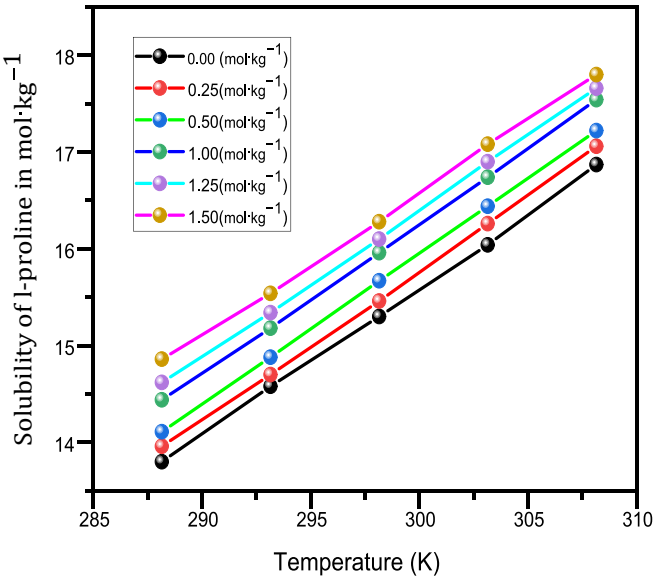


Fig. 3. Solubility alternation of l-proline in KCl-water within different concentration keeping fixed temperature (298.15 K).

Table 7. Amore stable 'ion-pair complex' [41,42] was formed between l-proline and KCl ions in solution due to the larger size of K^+ (radius = 1.52 Å) than Na^+ (radius = 1.02 Å) [35] that helps higher hydrogen bonding interaction to form ion-pair complex [41,42]and this enhance the solubility in KCl system rather than NaCl system.

The last conclusion can be explained on the ground of relationship between complex formation and thermochemical reactions i.e., exo /endo. In presence of electrolyte l-proline produce complex as shown above (equation 11). Water molecules associate together through intermolecular hydrogen bonding. With rising temperature greater number of water molecules become free due to crumble up those H-bonding and consequently water molecules are now interacted in a better way with the zwitterionic form of amino acid resulting rise in solubility.

4.2. Transfer free energy

Tables 5 and 6 and Fig. 9 reveal the variation of total transfer free energy values $\Delta G_t^0(i)$ with the different concentration of electrolyte in molality scale. Regarding the stability of the studied amino acid in an electrolytic solvent system, a number of interactions, including dipole–dipole, dispersion and cavity interaction, and other related parameters are taken into consideration.$\Delta G_t^0(i)$ is basically associated with the three parameters viz. $\Delta G_{t,dd}^0(i)$,$\Delta G_{t,cav}^0(i)$ and $\Delta G_{t,ch}^0(i)$ the values are summarized in Table 6. The results imply that the cavity contact supports to increasing the stability of l-proline due to attainment of larger size of NaCl (2.83 Å)/KCl (3.14 Å) [43] than water (2.74 Å) [34]. The energy shift resulting from the cavity's development for l-proline in electrolyte-water mixtures is more favourable. Now, dipole moment

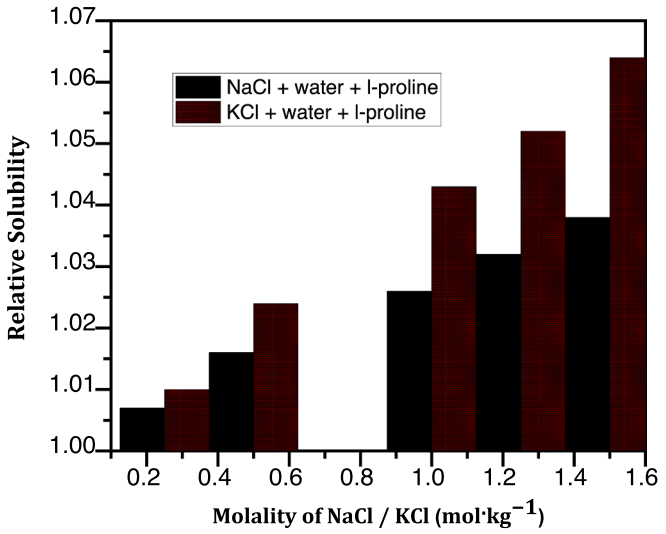


Fig. 4. Relative solubility of l-proline in NaCl + water and KCl-water at different composition of electrolytes at 298.15 K.

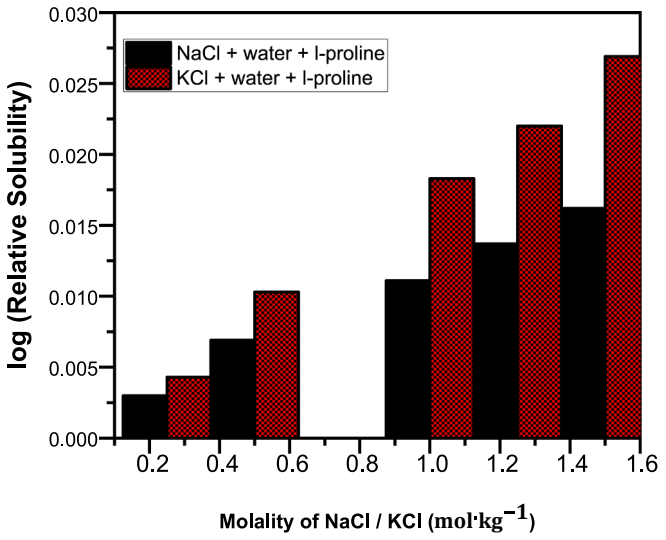


Fig. 5. log (Relative solubility) *vs.* molality (mol.kg^{-1}) of NaCl/KCl graph of l-proline in NaCl + water and KCl-water at different composition of electrolytes at 298.15 K.

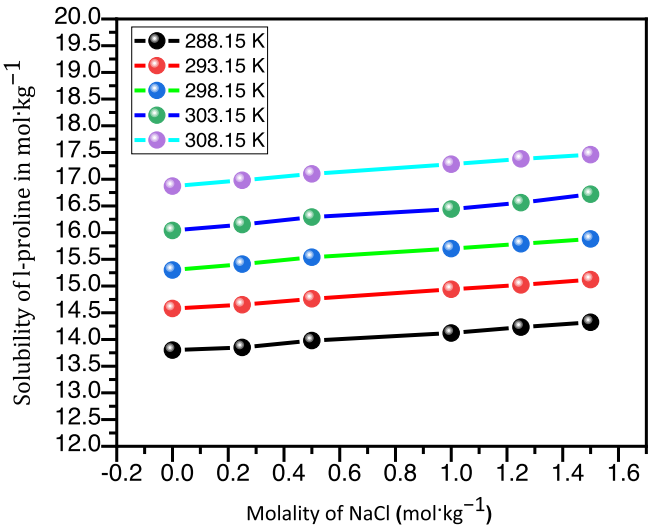


Fig. 6. Solubility variation of l-proline in NaCl-water solvent system at equidistant experimental temperature (K).

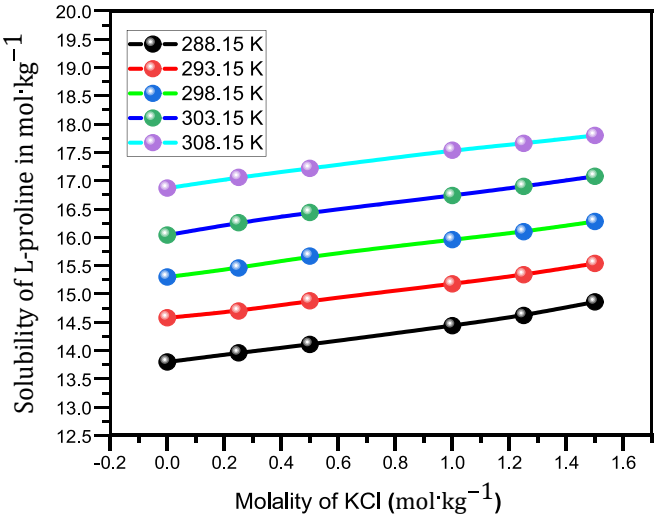


Fig. 7. Solubility variation of l-proline in KCl–water solvent system at five equidistant temperatures (K).

values of water, l-proline, KCl, NaCl are 1.84D, 5.86D, 10.27D [37] and 9D [20] respectively that helps to negative increment of $\Delta G^0_{t,dd}(i)$ values which stabilized amino acid in electrolytic media. Thus, the overall negative increment of $\Delta G^0_t(i)$ value which leads to the stabilization of l-proline in aqueous electrolyte media compare to pure aqueous solution.

The numerical values of $\Delta G^0_{t,ch}(i)$ were calculated after subtraction of $\Delta G^0_{t,dd}(i)$ and $\Delta G^0_{t,cav}(i)$ from $\Delta G^0_t(i)$. Fig. 10 shows the variation of this value ($\Delta G^0_{t,ch}(i)$) with concentration in molality scale.

In binary solvent solutions containing aqueous NaCl and aqueous KCl, we observe distinct chemical interactions. Hydrophilic connections are evident between the charged electrolyte ions and the charged amino (NH_3^+) and carboxyl groups (–COOH) of the zwitterionic amino acid. Conversely, the presence of these electrolytes results in hydrophobic interactions between the hydrophobic backbone of l-proline and water. In the current solvent system, hydrophilic interactions primarily govern solubility, while hydrophobic interactions play a major role in the variation of chemical transfer Gibbs free energy. In considering the chemical transfer Gibbs free energy, it is positive increment for l-proline in both binary electrolytes' solutions. But in case of NaCl, $\Delta G^0_{t,ch}(i)$ value shows less positive than in KCl-water solution which means l-proline is more stabilized in NaCl-water solution than in KCl-water solution system. This can be explained on the basis of ion-pair complex formation (Scheme 1).

As the concentration of NaCl or KCl in the system increases, the $\Delta G^0_{t,ch}(i)$ values gradually become positive, indicating the destabilization of l-proline due to chemical interactions with the solutes and solvent molecules. The amino acid experiences stabilization through cavity formation and dipole–dipole interactions, but other factors, particularly chemical interactions contributing to the total transfer free energy, lead to a positive increase in $\Delta G^0_{t,ch}(i)$, thereby destabilizing l-proline due to its interaction with the elevated concentration of NaCl or KCl in the NaCl/KCl–water solvent systems.

With increasing concentrations of NaCl/KCl in their aqueous mixtures, the solute molecules tend to form "ion-pair complexes" with the charged ions of the electrolytes in the solution. Consequently, there is increased contact between the nonpolar hydrocarbon backbone of l-

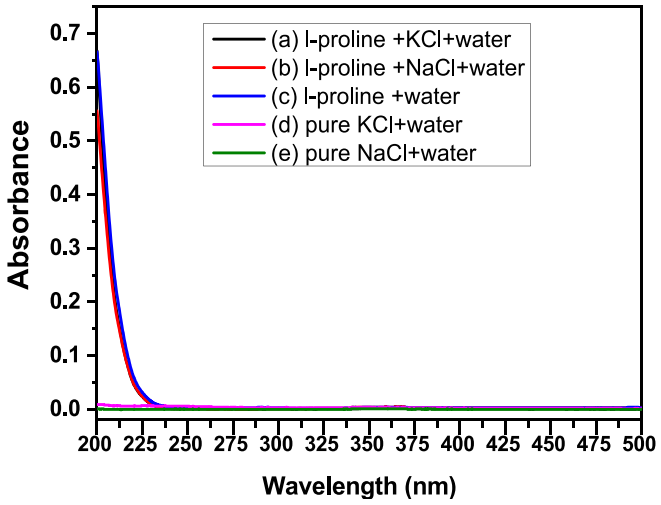


Fig. 8. Absorbance spectra of (a) l-proline in KCl + water solvent system; (b) l-proline in NaCl + water solvent system; (c) l-proline in pure water; (d) only pure KCl + water; (e) only pure NaCl + water.

Table 7
Salting-in constants of l-proline in NaCl + H_2O and KCl + H_2O at 298.15 K.

Amino Acid	K_{si} in NaCl + H_2O at 298.15 K	K_{si} in KCl + H_2O at 298.15 K
l-proline	0.01015 ± 5.46355E-4	0.01745 ± 7.09334E-4

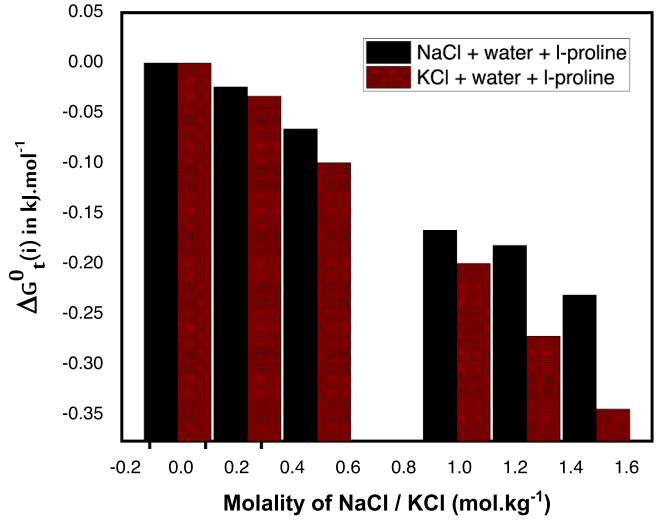


Fig. 9. Variation of transfer Gibbs free energy ($\Delta G_t^0(i)$) of l-proline in NaCl + water and KCl-water at different composition of electrolytes at 298.15 K.

proline and the electrolytes. This disrupts the hydrophobic hydration cosphere between water and solute molecules to a greater extent, resulting in a more significant increase in the positive $\Delta G_{t,ch}^0(i)$ value.

Notably, l-proline exhibits a more substantial positive increase in $\Delta G_{t,ch}^0(i)$ in the KCl-water system compared to the NaCl-water system, indicating that l-proline is more stable in the aqueous NaCl system. This heightened stability is attributed to the better match and more pronounced hydrophobic and electrostatic interactions between the relatively larger K^+ ion (1.52 Å) and l-proline (4.97 Å), resulting in the formation of a more stable "ion-pair complex" [$M^+\{^-OOCC_4H_7(NH_2^+)\}$ Cl^-] [Where, M = Na^+/K^+]. In contrast, the ion-pair formed by the smaller Na^+ ion (1.02 Å) and the same amino acid is less stable due to the mismatch in sizes and interactions.

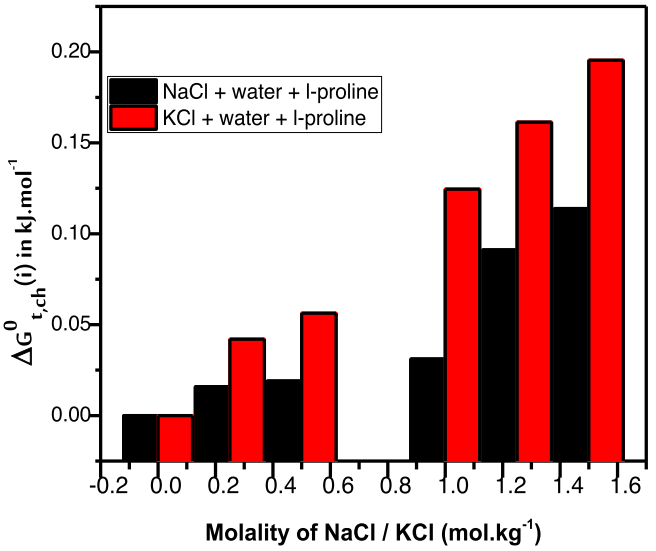


Fig. 10. Variation of chemical transfer Gibbs free energy ($\Delta G_{t,ch}^0(i)$) of l-proline in NaCl + water and KCl-water at different composition of electrolytes at 298.15 K.

4.3. Transfer entropies

The entropy of transfer, $T\Delta S_t^0(i)$ like $\Delta G_t^0(i)$ is composed of cavity, dipole–dipole and different other short range chemical interactions effects, i.e.:

$$T\Delta S_t^0(i) = T\Delta S_{t,cav}^o(i) + T\Delta S^0{}_{t,d-d}(i) + T\Delta S^0{}_{t,ch}(i) \quad (13)$$

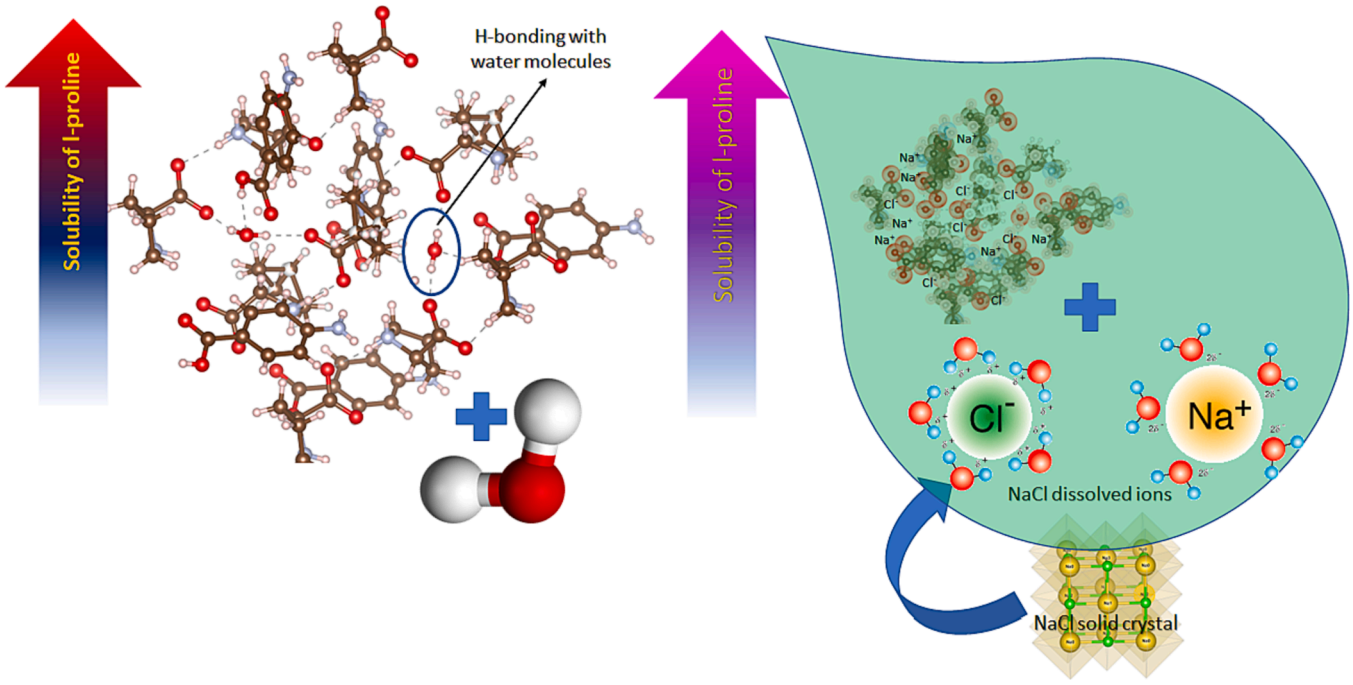
The first two terms are corresponding to the entropy change due to cavities formation for incorporating l-proline and dipolar interaction with solvent molecules respectively. If we consider both effects together then there would be negative increment in the $T\Delta S_t^0(i)$ $T\Delta S_t^0(i)$ versus mole fraction of NaCl/KCl electrolyte for l-proline.

To simplify the calculation, we ignored the interaction of dipole and induced dipole. This type of complex variations can be seen because different of chemical interactions between the used water solvent molecules induced by the l-proline molecule. This type of variation of interactions were also reported in several articles [20,33].$T\Delta S_t^0(i)$ and $T\Delta S_{t,ch}^0(i)$ values are tabulated in Table 6. $T\Delta S_{t,ch}^0(i)$ values for l-proline are estimated by subtraction of $T\Delta S_{t,cav}^0(i)$, and $T\Delta S_{t,d-d}^0(i)$) from $T\Delta S_t^0(i)$. Fig. 11 shows the variation of total transfer entropy values in both electrolytic systems at specific temperature while Fig. 12 shows the $T\Delta S_{t,ch}^0(i)$) values for l-proline in water electrolytic systems.

Solvent-solvent interaction is considered to explain the transfer entropies either it be total or chemical. In electrolytic environment l-proline has an ability to produce ion-pair complex [$M^+\{^-OOCC_4H_7(NH_2^+)\}$ Cl^-] [where, M = Na^+/K^+] between amino acid and electrolyte molecules resulting more water molecules will be free in solution to interact themselves through hydrogen bonding causing enhancing solvent–solvent interaction which in turn showing lesser randomness of solvent molecules and negative values of both total and chemical transfer entropies. In considering the both electrolytic solutions namely water-NaCl and water-KCl it was found that for 2nd one shows more negative $T\Delta S_{t,ch}^0(i)$ values in the binary solution due to proper size matching during ion-pair complex formation. Salting in effect as well as rising of solubility also gives support to this fact.

5. Conclusion

In conclusion, this study investigated the solubility behavior of



Scheme 1. Variation of solubility of l-proline in pure water and electrolytic solutions.

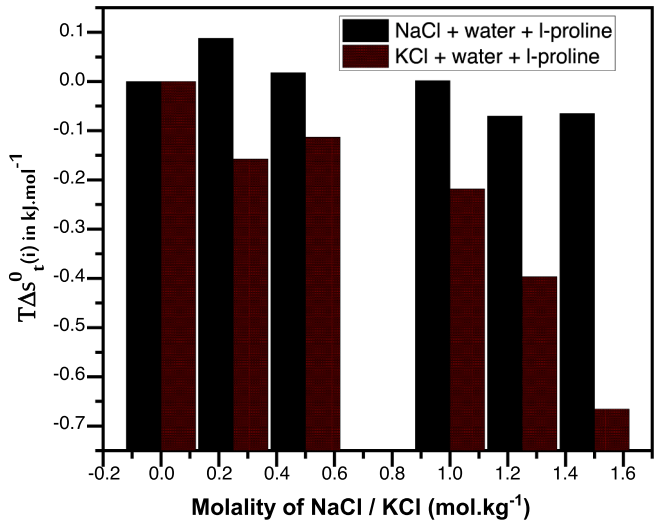


Fig. 11. Variation of transfer entropy ($T\Delta S_t^0(i)$) of l-proline in NaCl + water and KCl-water at different composition of electrolytes at 298.15 K.

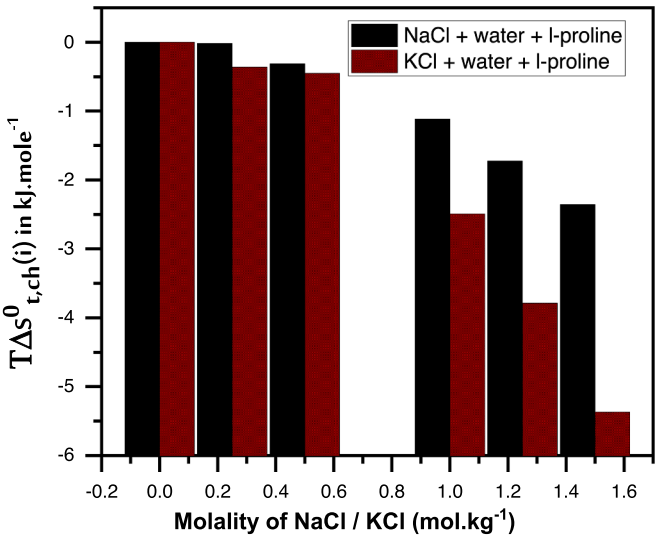


Fig. 12. Variation of chemical transfer entropy ($T\Delta S_{t,ch}^0(i)$) of l-proline in NaCl + water and KCl-water solvent system at 298.15 K.

amino acids in aqueous solutions with the presence of electrolytes, focusing on the solvation energies which are verified by temperature and concentration variations. The experimental findings specifically revealed that the protogenic amino acid l-proline exhibited enhanced solubility in the presence of the tested electrolytes compared to pure water. Furthermore, the research indicated that l-proline displayed higher solubility in KCl relative to NaCl at any concentrations and temperatures. Results found that the chemical transfer free energy ($\Delta G_{t,ch}^0(i)$) increases is more positive for water-KCl binary solution than water-NaCl binary system due to lesser solute–solvent interaction in water-KCl solvent system. On the other hand, chemical transfer entropies show negative increment with increasing both electrolyte concentration and this variation is illustrated based on solvent–solvent interaction. In case of water-KCl solvent system chemical transfer entropies is more negative than in water-NaCl solvent system. This might be due higher complexing nature of KCl with l-proline molecules so that amino acid molecules are easily trapped by KCl and hence more water molecules will be in the system and then water molecules associated quickly among them through intermolecular hydrogen bonding to decrease the overall entropy of the system. Further investigations can delve into exploring the solubility trends, other relating thermodynamical parameters and extend the study to other amino acids in different other environmentally friendly conditions, providing valuable insights into the solvation behavior of amino acids types of molecules and expanding the knowledge base in this field.

CRediT authorship contribution statement

Avishek Saha: Conceptualization, Investigation. **Kalachand Mahali:** Conceptualization, Investigation. **Sintu Ganai:**

Conceptualization, Investigation. **Puspal Mukherjee:** Conceptualization, Investigation. **Nabeen K. Shrestha:** . **A.M.A. Henaish:** . **Jahangeer Ahmed:** . **Simanta Kundu:** Conceptualization, Investigation. **Sanjay Roy:** Writing – original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2023.123352.

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