Canadian Journal of Chemistry

Research Article

Thermodynamic analysis for the dissolution of two similar amino acids in sodium sulfate aqueous solution

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Abstract

In the current work, the analyti cal static gravimetric technique was used to assess the solubilities of DL-α-amino butyric acid and DL-valine in an aqueous binary solvent mixture of sodium sulfate (Na_2SO_4) under equilibrium saturation conditions in between temperature range 288.15 and 308.15 K. Different thermodynamic factors along with transfer Gibbs energetics and entropies under standard conditions were estimated by using computational as well as theoretical method by using the experimental solubilities. Several modes of interactions that occur during solvation were also explained. The manner that solvent molecules of solute amino acids are surrounded in the aforementioned medium employed during the process is taken into consideration. Amino acids become more soluble as the temperature rises. The study also helps us to reach the conclusion that physical properties of electrolyte (Na_2SO_4), mixed solvent, and the size of the amino acids' molecules are the main governing factors for the chemical stability as well as other thermodynamic and physical property like solubility of solute amino acids.

Key words: solubility, DL-α-amino butyric acid, DL-valine, free energy, entropy

1. Introduction

Solvation phenomena associated with solubility and solvation thermodynamics of the biomolecules play a key role in the field of industrial, medical, and pharmaceutical research areas. Researchers from all around the world have been attempting for a long time to reveal out the specifics of solvation-related consequences of biomolecules, particularly those employed in various fields of medicine.[1–5] Body protein as well as other vital nitrogen-containing substances including peptide hormones, creatine, and a few neurotransmitters cannot be produced without amino acids. Amino acids aid in the digestion of food and the growth and repair of body tissue. Additionally, it gives off energy and keeps our hair, skin, and nails in good condition. It aids in strengthening our immune system and building muscle. Additionally, it aids in maintaining a healthy digestive tract. To understand all such biological phenomenon of amino acids a detail study of solubility and solvation thermodynamics become very needful. On the other hand, to meet standards for high membrane permeability and water solubility, drugs must have the right balance between polarity and hydrophobicity. As a result, methods for predicting solubilities of drug molecules in water are an important research field for drug design. Therefore, understanding numerous complex interactions and providing a pathway to designing a new and effective medicine are made much easier with knowledge of solution chemistry. Furthermore, the solubility of pharmaceutical products in water shows broad tendencies for the rate of dissolution; poor solubility is typically correlated with a relatively slothful rate of dissolution.[6] The regulated distribution of an active pharmaceutical ingredient is achieved via an osmotic drug delivery system, which basis on the concepts of osmotic pressure which in turn depends on the solubility. The concept of solubility is also very needful for the industrial areas like fertilizer,[7] ceramics,[8] cement,[9] food processing,[10] etc. Researchers are doing their work on amino acids solubility in the commonly usable solvent systems like binary aqueous (l-glycine in aqueous solution),[11] binary non-aqueous (α-amino acids in DMSO),[12] binary or ternary aqueous (l-proline in ammonium sulfate solution),[13] and in many electrolytes (KCl, $NaNO_3$, etc.)[14] solvents systems and from those they have tried to find out the solubility and solvation thermodynamics only because the solubility and the corresponding thermodynamic parameters control and diversify working attitude of the biomolecules. The solvation-based thermodynamics study also encourages the extraction of proteins in their purest form from various sources. For these reasons, it is become very needful to gather more knowledge on learning about the solvable capabilities of different types of amino acids in different types of solvent systems either in presence or in absence of electrolyte and from last few years the study on solubility and related thermodynamical properties of any amino acids is very much attractive for research purpose.[15–18] The solvation thermodynamical behavior of so-

lute amino acids was also observed in various conditions like temperature, polarity, acidity–basicity, and ionic nature of the experimental co-solvent or electrolyte. On the ground of physical characteristics of electrolytes, equilibrium solubilities change dramatically.[19–25] The capability of electrolytes used in experimental media on conformational alternation and orientation of protein monomer unit molecules, produce profound influence on variety of thermodynamic variables, including dipole–dipole interactions, cavity formation, enthalpy, and crucial hydrophilic, hydrophobic, and acid–base interactions. They all work together to influence the internal biological atmosphere and bodybuilding components turning beneath and broadening processes.[26–28] For these reasons, the importance on this research area goes on increasing bit by bit mainly focusing on how bio-organic compounds like amino acids fare in solutions of various salts. Both DL-α-amino butyric acid and DL-valine are integral components of the complex network of biological processes in the body. While DL-α-amino butyric acid is less well studied compared to some other amino acids, ongoing research may provide further insights into its functions and potential applications. Valine, being an essential amino acid, is vital for various physiological processes and is particularly important for individuals who need to obtain it through their diet.

It is important to note that the specific use of sodium sulfate in biological applications depends on the context and the desired outcome of the experiment or process. While sodium sulfate itself is not a biologically active molecule, its properties make it a useful tool in various laboratory techniques related to molecular biology, biochemistry, and cell biology.

The detail dissolution thermodynamics under several experimental circumstances is still scarce. Therefore, in this present study investigations are concentrated on the thermodynamic point of view to boost the knowledge of mentioned homologous acids in sodium sulfate solution. Both transfer free energy and transfer entropy are calculated at 298.15 K throughout the investigation.

2. Experimental part

2.1. Chemicals and refinement

DL-α-amino butyric acid (melting point: 452 K) and DL-valine (melting point: 568.5 K)[29] (>99.0%, Sigma-Aldrich) were perched and dried in an entirely vacuum desiccator below their melting points (at 400.15 K) for a week. Temperature-controlled oven was employed for 10 days for drying of Na_2SO_4 (>98% G.R. Grade) by maintaining temperature at 430.15 K. After dropping down temperature to normal temperature (at room temperature) Na_2SO_4 was used for making solution having different molality (0.0, 0.5, 1.0, 1.5, and 2.0 mol kg^{-1}) with such triple distilled water made in our own lab, having a conductivity of 0.9 μS/cm.

2.2. Preparations of saturated solutions

The aqueous Na_2SO_4 salt solutions were made ready for the experiment. An excess amount (more than soluble amount at a particular experimental temperature) of each amino acid was added to the solvent combinations in stoppered glass jars (Borosil) to set up the saturated solutions of the amino acids. They spent a full day in a shaking machine (200–250 rpm) to achieve uniformity. After that the equilibrium mixtures were taken for settle down for 12 h. For our investigation, 10 sets (5 for DL-α-amino butyric acid and 5 for DL-valine) of aqueous electrolytic salt solutions under waterlogged condition were made according to tabulated equidistance (5 K each) temperature (288.15–308.15 K) and the mixtures were swirled continuously for a whole day to accomplish the constancy in a temperature controllable digital heating and cooling water bath (purchased from B.S. Scientific India) having a temperature accuracy of ±0.10 K.

2.3. Measurement of solubility

The solubility of the amino acids in the solution was assessed through a systematic gravimetric analysis.[24,30] Each saturated solution was given 6 h to quiet the undissolved solutes prior to sampling. An HPLC disposable filter paper carrying pore size 0.22 m was then used to filter the top 3 mL of each solution that had been taken individually using dry pipettes. After being promptly transferred into a glass jar, the filtrate was weighed. The filtrate was entirely evaporated to dryness in a heating chamber before being dried at 365.15 K in a temperature-controlled drying oven to get amino acid crystals. To combat water absorption, it was then chilled in a dehydrator using silica gel for 12 h, and finally the dried solutes were weighed. The process performed until a constant weight achieved of the dried sample containing vessel. In our experiment we have taken the weight four times to get the constant weight.

3. Theoretical section

The solubility of the solutes was estimated mathematically, similar to the earlier research studies.[31–33] Assume that the weights of electrolyte and empty vessel are W_1 and W_2 g, respectively, and the weight of aqueous electrolyte amino acid solution with vessel is W_3 g. If the complete dried experimental mixture weight in vessel is taken as W_4 g, then amount of evaporated water is $(W_3 - W_4)$ and amount of amino acid present in the mixture is $(W_4 - W_2 - W_1)$ g.

So, solubility of experimental amino acids is as follows: $(W_4 - W_2 - W_1) \times 1000/(W_3 - W_4) \times M_1$ mole per kg of water, where M_1 is taken as molar mass of the amino acids.

Table 1 displays the determined saturation solubilities of the DL-Aba and DL-valine solutes in mol kg^{-1} of water in various aqueous electrolytes at five temperatures as tabulated below. These solubility values were determined to be reproducible to within 2.7%.

With the help of eq. 1 as given below, at certain experimental setting we evaluated[1,28,33] the solution Gibbs energies (ΔG_s^0) of amino acids on molal scale.

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

where γ is the molal activity coefficient and "S" is the saturated solubility of the DL-α-amino butyric acid and DL-valine

Table 1. Solubility of DL-α-amino butyric acid and DL-valine with standard uncertainties ($\pm$) in water and water + Na_2SO_4 in different compositions of Na_2SO_4 at five temperatures[#] at atmospheric pressure, $p = 0.1$ MPa[a] ($\pm$ standard deviation in solubility results).

	Solubility in mol kg^{-1}				
Molality of salt (mol kg^{-1})	0.0	0.5	1.0	1.5	2.0
DL-α-amino butyric acid in Na_2SO_4 + H_2O					
288.18 K	2.150 ± 0.027	1.940 ± 0.015	1.630 ± 0.018	1.302 ± 0.025	1.018 ± 0.021
293.15 K	2.170 ± 0.023	2.024 ± 0.013	1.718 ± 0.012	1.392 ± 0.020	1.030 ± 0.010
298.15 K	2.268 ± 0.012	2.110 ± 0.018	1.806 ± 0.030	1.420 ± 0.028	1.068 ± 0.023
303.15 K	2.408 ± 0.019	2.245 ± 0.022	1.904 ± 0.026	1.546 ± 0.019	1.202 ± 0.021
308.15 K	2.605 ± 0.016	2.401 ± 0.020	2.108 ± 0.013	1.702 ± 0.018	1.348 ± 0.024
DL-valine in Na_2SO_4 + H_2O					
288.18 K	0.560 ± 0.014	0.432 ± 0.026	0.342 ± 0.027	0.265 ± 0.028	0.182 ± 0.032
293.15 K	0.656 ± 0.017	0.520 ± 0.017	0.406 ± 0.025	0.324 ± 0.026	0.205 ± 0.026
298.15 K	0.762 ± 0.012	0.604 ± 0.022	0.472 ± 0.028	0.382 ± 0.029	0.307 ± 0.022
303.15 K	0.782 ± 0.018	0.648 ± 0.024	0.506 ± 0.029	0.422 ± 0.030	0.346 ± 0.027
308.15 K	0.830 ± 0.011	0.702 ± 0.013	0.560 ± 0.021	0.438 ± 0.019	0.384 ± 0.028

Note: Standard uncertainties u are $u(T) = 0.10$ K[#] and $u(m) = 0.01$ mol kg^{-1}, and relative uncertainties in pressure $u_r(p)$[a] $= 0.02$.

in mol kg^{-1}. In our current research, our main focus revolves around the transfer Gibbs free energy, with the aim of establishing its connection to solubility outcomes and getting idea on the dissolution mechanism of amino acids. While evaluating the Gibbs free energy of solution, we acknowledge the potential influence of the activity coefficient (γ). However, for the purposes of this study, we are assuming a constant activity coefficient (γ) equal to one.[1,2,21,22,34]

Our primary interest lies in understanding the nature of variation of transfer Gibbs free energy as it relates to solubility results and describing the dissolution process of amino acids. In the calculation of the Gibbs free energy of solution, the activity coefficient (γ) may play a role, but in our current investigation, we treat the activity coefficient (γ) as a constant value like the previous studied.[1,2,21,22]

Furthermore, our main objective in this study is to determine the standard total transfer Gibbs energies for biomolecules, specifically amino acids in experimental sulfate aqueous solutions. 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 amino acids in Na_2SO_4 aqueous solvent and water, respectively), so

$$\Delta G_t^0(i) = -RT\ln(m_s\gamma_s) + RT\ln(m_R\gamma_R) = -RT\ln\left(\frac{m_s\gamma_s}{m_R\gamma_R}\right) = -RT\ln\left(m_s/m_R - RT\ln\left(\frac{\gamma_s}{\gamma_R}\right)\right)$$

Hence in the calculation of transfer Gibbs free energy, the activity coefficient factor, $-RT\ln\left(\frac{\gamma_s}{\gamma_R}\right)$ (s stands for aqueous Na_2SO_4 solution, whereas R for reference solvent: H_2O), tends to be negligibly small. Hence, it is reasonable to assume that the contribution of the activity coefficient can be ignored in our study for estimating the total transfer Gibbs free energy.[1,2,21,22,34]

As the tabulated five different equally spaced temperatures least square was employed for calculating free energies of solution as display in Table 2 by using eq. 2 as

$$\Delta G_s^0 = a + bT + cT\ln T \quad (2)$$

where T is the absolute temperature, while a, b, and c are the coefficients, and the values are summarized in Table 3. Within the range > 0.04 units, the values are determined to accurately reflect the experimental results.

Standard transfer Gibbs energies ΔG_t^0 of DL-α-amino butyric acid and for DL-valine in aqueous-to-aqua-salt solutions were determined at 298.15 K by using eq. 3,

$$\Delta G_t^0(i) = \left(s\Delta G_{sol}^0(i) - {}_R\Delta G_{sol}^0(i)\right)$$

i.e.,

$$\Delta G_t^0(i) = (a_s - a_R) + (b_s - b_R)T + (c_s - c_R)T\ln T - RT\ln(M_s/M_R) \quad (3)$$

here the subscript "s" stands for aqueous Na_2SO_4 mixtures, while "R" refers to the reference solvent (water). M_R, M_s are the molar masses of the pure and mixed electrolyte solvents, respectively. $\Delta G_t^0(i)$ values of DL-α-Aba and for DL-valine are evaluated and presented in Table 3. The standard uncertainties in determining the $\Delta G_t^0(i)$ values are found maximum as $\pm$0.03 kJ mol^{-1}.

It is true that the $\Delta G_t^0(i)$ is a baffling value includes various transfer free energy terms i.e., it is the total of transfer free energies due to cavity construction interactions ($\Delta G_{t,cav}^0(i)$) owing to the formation of cavities for DL-α-amino butyric acid and for valine in aqueous electrolyte solvents. Free energies ($\Delta G_{t,d-d}^0(i)$) crop up due to inter-association existing between zwitterionic

Table 2. Gibbs energies of solutions (ΔG_S^0) on molal scale in their respective solubilities of DL-α-amino butyric acid and DL-valine in aqueous mixtures of Na_2SO_4 in different compositions of Na_2SO_4 at different temperatures (K).

288.18 K		293.15 K		298.15 K		303.15 K		308.15 K	
S (mol kg^{-1})	ΔG_s^0 (*i*) (kJ mol^{-1})	S (mol kg^{-1})	ΔG_s^0 (*i*) (kJ mol^{-1})	S (mol kg^{-1})	ΔG_s^0 (*i*) (kJ mol^{-1})	S (mol kg^{-1})	ΔG_s^0 (*i*) (kJ mol^{-1})	S (mol kg^{-1})	ΔG_s^0 (*i*) (kJ mol^{-1})
DL-α-amino butyric acid in $Na_2SO_4 + H_2O$									
2.150	−1.8338	2.170	−1.8882	2.268	−2.0299	2.408	−2.2149	2.605	−2.4529
1.940	−1.5876	2.024	−1.7185	2.110	−1.8509	2.245	−2.0383	2.401	−2.2439
1.630	−1.1705	1.718	−1.3189	1.806	−1.4653	1.904	−1.6230	2.108	−1.9106
1.302	−0.6322	1.392	−0.8061	1.420	−0.8692	1.546	−1.0981	1.702	−1.3625
1.018	−0.0427	1.030	−0.0720	1.068	−0.1631	1.202	−0.4637	1.348	−0.7651
DL-valine in $Na_2SO_4 + H_2O$									
0.560	1.3891	0.656	1.0275	0.762	0.6738	0.782	0.6198	0.830	0.4774
0.432	2.0108	0.520	1.5938	0.604	1.2498	0.648	1.0935	0.702	0.9065
0.342	2.5704	0.406	2.1969	0.472	1.8610	0.506	1.7169	0.560	1.4855
0.265	3.1815	0.324	2.7468	0.382	2.3855	0.422	2.1745	0.438	2.1149
0.182	4.0816	0.205	3.8624	0.307	2.9273	0.346	2.6749	0.384	2.4521

Table 3. The values of coefficients *a*, *b*, *c*, and ΔG_t^0 (*i*), $T\Delta S_t^0$ (*i*) for solute DL-α-amino butyric acid and DL-valine in the presence and absence of Na_2SO_4 in different compositions at 298.15 K.

Molality of salt (mol kg^{-1})	*a* (kJ mol^{-1})	*b* (kJ mol^{-1} K^{-1})	*c* (kJ mol^{-1} K^{-1})	ΔG_t^0 (*i*) (kJ mol^{-1})	$T\Delta S_t^0$ (*i*) (kJ mol^{-1})
DL-α-amino butyric acid in $Na_2SO_4 + H_2O$					
0.0	−201.21	4.6528	−0.69937	0.000	0.000
0.5	40.41	−0.7355	0.10415	−0.079	2.129
1.0	−137.97	3.2700	−0.49357	0.273	1.607
1.5	−166.62	3.9222	−0.59085	0.696	1.539
2.0	−372.07	8.5631	−1.28402	1.302	2.157
DL-valine in $Na_2SO_4 + H_2O$					
0.0	388.96	−8.4669	1.25751	0.000	0.000
0.5	346.43	−7.4449	1.10349	0.392	2.998
1.0	259.49	−5.4845	0.81097	0.893	2.773
1.5	475.95	−10.3295	1.53419	1.250	3.248
2.0	372.75	−7.7969	1.15486	1.848	5.553

amino acids (DL-α-Aba or DL-valine) and solvated electrolyte molecules. Chemical transfer free energies ($\Delta G_{t,\mathrm{cav}}^0$ (*i*)) are result of chemical inter-associations like acid–base, dispersion, dipole–dipole, hydrophilic/hydrophobic hydration, and structural properties of the experimental constituting molecules.

ΔG_t^0 (*i*) is really the sum of few terms as given below:

$$\Delta G_t^0(i) = \Delta G_{t,\mathrm{cav}}^0(i) + \Delta G_{t,d-d}^0(i) + \Delta G_{t,\mathrm{cav}}^0(i) \quad (4)$$

In this scenario, values where all members of solution except electrolyte are considered to be rigid spheres as specified by their separate diameters were determined $\Delta G_{t,\mathrm{cav}}^0$ (*i*) values using the scaled particle theory[26,34–38] (Table 4). Equation 5 was put in estimating interactions arising out due to cavity construction as follows:[36,37]

$$\Delta G_{\mathrm{cav}}^0(i) = G_C + RT\ln\left(\frac{RT}{V_S}\right) \quad (5)$$

where

$$G_C = RT\left[-\ln(1-Z) + \left\{\frac{3X}{1-Z}\right\}\sigma_x + \left\{\frac{3Y}{1-Z}\right\}{\sigma_x}^2 + \left\{\frac{9X^2}{2(1-Z)^2}\right\}{\sigma_x}^2\right.$$

$$Z = \pi N_A/6V_S\left(Z_R{\sigma_R}^3 + Z_S{\sigma_S}^3\right)$$

$$X = \pi N_A/6V_S\left(Z_R{\sigma_R}^2 + Z_S{\sigma_S}^2\right)$$

$$Y = \pi N_A/6V_S\left(Z_R\sigma_R + Z_S\sigma_S\right)$$

$$V_S = M_S/d_S$$

where N_A is Avogadro's number, Z_R is the mole fraction of water, Z_S is the mole fraction of electrolytes, σ_x is the hard

Table 4. Values of solvent mole fraction of salt, water, mean mol. weight of electrolyte solvent, density, molar volume, solvent diameters (σ_s), σ_{s-x}, μ_s, $\sigma_{s-x} = \frac{1}{2}(\sigma_s + \sigma_x)$ and isobaric thermal coefficient (α) and dipole moment (D) of the $H_2O + Na_2SO_4$ systems at 298.15 K.

Molality of salt (mol kg^{-1})	Mole fraction (z_s)	Mole % salt	Mole fraction (z_R)	Molar mass (M_S) (g/mol)	d_s (g/cm^3)	Molar volume (V_s) (cm^3/mol)	Dipole moment (μ_s) (Debye)	σ_s (nm)	σ_{s-x} (nm) (DL-α-Aba)	σ_{s-x} (nm) (DL-val)	α ($\times 10^3$) (K^{-1})
Water–Na_2SO_4 system											
0.0	0.000	0.00	1.000	18.015	0.997*	18.069	1.831*	0.274	0.466	0.483	0.257*
0.5	0.009	0.90	0.991	19.119	1.012	19.179	1.820	0.277	0.468	0.485	0.257
1.0	0.018	1.80	0.982	20.211	1.026	19.691	1.809	0.279	0.469	0.486	0.257
1.5	0.026	2.60	0.974	21.277	1.041	20.445	1.800	0.281	0.470	0.487	0.257
2.0	0.035	3.50	0.965	22.331	1.055	21.169	1.789	0.284	0.471	0.488	0.257

Note: $u(M) = \pm 0.01$, $u(M_s) = \pm 0.0002$, $u(d_s) = \pm 0.0002$, $u(\sigma_s) = \pm 0.0001$, $u(\mu_s) = \pm 0.0002$, (u for uncertainty); dipole moment of Na_2SO_4 is 0.64 D (from DFT study);[46] *for reference,[27] calculated diameter of Na_2SO_4 is 5.53 Å.[46]

sphere diameter of solute DL-α-Aba/DL-valine, σ_R is the diameter of aqueous molecule considering hard sphere, σ_s is the diameter of co-solvent (solvated electrolyte molecule) accounting as hard sphere, V_S is the molar volume, M_s is the molar mass, and d_s is the density of aqua-Na_2SO_4 solutions in molar scale. The values of these parameters are shown in Table 4.

Therefore, $\Delta G^0_{t,cav}(i)$ signifies the difference as eq. 6.[32,38]

$$(6)\quad \Delta G^0_{t,cav}(i)_s\,\Delta G_t(\text{cav}) - {}_R\,\Delta G_t(\text{cav}) = ({}_s\,\Delta G_C - {}_R\,\Delta G_C) + RT\ln(V_R/V_S)$$

The following values were calculated using the Keesom orientation expression (eq. 7) for this study:

$$(7)\quad \Delta G^0_{t,d-d}(i) = \left(s\Delta G^0_{d-d}(i) - {}_R\Delta G^0_{d-d}(i)\right)$$

In solution, ${}_s\,\Delta G_{d-d}(i)$ is presented as

$$(8)\quad {}_s\,\Delta G_{d-d}(i) = -(8\Pi/9)N^2\mu_s^2\mu_x^2\sigma_{s-x}^{-3}(kT)^{-1}V_x^{-1} = A/TV_s$$

$$A = -(8\Pi/9)N^2\mu_s^2\mu_x^2\sigma_{s-x}^{-3}(k)^{-1}$$

and

$$V_s = M_s/d_s$$

where N is Avogadro's number, μ_s and μ_x are dipole moments of electrolyte solvent system and amino acid molecules (Table 4), σ_{s-x} is the diameter of attractive or repulsive interactions between the solvent and DL-α-amino butyric acid molecules and it is equivalent to $\frac{1}{2}(\sigma_s + \sigma_x)$,[26,38] where σ_s and σ_x are hard sphere diameter of hydrated electrolyte and single DL-α-Aba and DL-valine molecule, respectively. Values of μ_s and σ_s in different experimental electrolyte solutions are shown in Table 4. Such values were then multiplied with X_{s1} to get the values of $\Delta G^0_{t,d-d}(i)$ in mole fraction scale.[26,39,40] X_{s1} can be presented as

$$(9)\quad X_{s1} = X_s\left(\mu_s/\sigma_s^3\right)/\left(\mu_R/\sigma_R^3\right)$$

Here, X_{s1} represents the actual mole fraction participation due to dipole–dipole interaction effect.

To find $\Delta G^0_{t,ch}(i)$ the values of $\Delta G^0_{t,cav}(i)$ and $\Delta G^0_{t,d-d}(i)$ subtract from $\Delta G^0_t(i)$ and the results are shown in Table 5.

Similarly,

$$(10)\quad \Delta S^0_t(i) = (b_R - b_s) + (c_R - c_S)(1 + \ln T) + R\ln(M_s/M_R)$$

The letters S and R stand for aqueous electrolyte mixes and pure water, respectively. M_s and M_R stand for the molar masses of mixed electrolyte solvents and water, respectively. The values of total transfer entropies are displayed in Tables 3 and 5. The maximum measurement error was calculated 0.016 kJ K^{-1} mol^{-1}.

Here, $\Delta S^0_{t,d-d}(i)[= ({}_s\,\Delta S_{t,\,d-d}(i) - {}_R\,\Delta S_{t,\,d-d}(i)]$ and was measured by using Keesom Orientation expression.[41,42]

The expression of $\Delta S^0_{d-d}(i)$ is given as

$${}_s\,\Delta S_{d-d}(i) = -\left\{\delta_s\,\Delta G_{d-d}(i)/\delta T\right\}_p$$

i.e.,

$$(11)\quad T_s\,\Delta S_{t,\,d-d}(i) = {}_s\,\Delta S_{t,\,d-d}(i)[1 + T\alpha]$$

where α is known as isobaric thermal coefficient of a solvent. The value of "α" was estimated by using eq. 12.[26,43]

$$(12)\quad \alpha = \delta(lnV_s/\delta T)_P = -(\delta lnd_s/\delta T)_P$$

The variations in enthalpies for the formation of cavity during the transfer from aqueous to aqueous–Na_2SO_4 solutions are estimated by using eqs. 13 and 14.[14,43–45]

$$(13)\quad \Delta H^0_{t,cav}(i)_s\,\Delta H^0_{cav}(i) - {}_R\,\Delta H^0_{cav}(i)$$

$$(14)\quad \Delta H^0_{cav}(i) = (A + H + K + E) \times B$$

where $A = (\Pi N_A/6V_s) \times \left(Z_R\sigma_R{}^3 + Z_S\sigma_S^3\right)$; $B = \sigma_S RT^2/1 - A$;

$$H = \sigma_x \times 3Y/1 - A;\ K = \sigma_x \times 3X/1 - A$$

$$E = 9\sigma_x{}^2 \times X^2/(1 - A)^2$$

$$X = (\Pi N_A/6V_s) \times \left(Z_R\sigma_R{}^2 + Z_S\sigma_S^2\right)$$

and

$$Y = (\Pi N_A/6V_s) \times (Z_R\sigma_R + Z_S\sigma_S);\ \Pi = 22/7$$

The values of $\Delta H^0_{t,cav}(i)$ in kJ mol^{-1} are shown in Table 5.

4. Discussion

4.1. Solubility

Solubilities of DL-α-Aba at different temperatures in aqueous and aqueous Na_2SO_4 solutions at various molalities are

Table 5. Gibbs energies of transfer $\Delta G_t^0(i)$, $\Delta G_{t,\mathrm{cav}}^0(i)$, $\Delta G_{t,d-d}^0(i)$, $\Delta G_{t,\mathrm{ch}}^0(i)$, and enthalpy, $\Delta H_{t,\mathrm{cav}}^0(i)$ and entropies of transfer $T\Delta S_t^0(i)$, $T\Delta S_{t,\mathrm{cav}}^0(i)$, $T\Delta S_{t,d-d}^0(i)$, and $T\Delta S_{t,\mathrm{ch}}^0(i)$ of DL-α-Aba and DL-valine in different compositions of Na_2SO_4 at 298.15 K in kJ mol^{-1}.

Molality (mol kg^{-1})	$\Delta G_t^0(i)$	$\Delta G_{t,\mathrm{cav}}^0(i)$	$\Delta G_{t,d-d}^0(i)$	$\Delta G_{t,\mathrm{ch}}^0(i)$	$T\Delta S_t^0(i)$	$\Delta H_{t,\mathrm{cav}}^0(i)$	$T\Delta S_{t,\mathrm{cav}}^0(i)$	$T\Delta S_{t,d-d}^0(i)$	$T\Delta S_{t,\mathrm{ch}}^0(i)$
DL-α-amino butyric acid $Na_2SO_4 + H_2O$									
0.0	0.000	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000
0.5	−0.079	−0.619	0.067	0.473	2.129	−0.578	0.041	0.072	2.097
1.0	0.273	−0.879	0.237	0.915	1.607	−1.054	−0.175	0.255	1.527
1.5	0.696	−1.241	0.458	1.479	1.539	−1.429	−0.188	0.493	1.234
2.0	1.302	−1.563	0.748	2.117	2.157	−1.748	−0.185	0.805	1.537
DL-valine $Na_2SO_4 + H_2O$									
0.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.5	0.392	−0.647	0.059	0.980	2.998	−0.632	0.015	0.065	2.918
1.0	0.893	−0.919	0.212	1.600	2.773	−1.154	−0.235	0.228	2.780
1.5	1.250	−1.297	0.410	2.137	3.248	−1.565	−0.268	0.441	3.075
2.0	1.848	−1.633	0.699	2.812	5.553	−1.913	−0.280	0.720	5.113

Note: Diameter of DL-α-Aba 0.658 nm,[39] DL-valine 0.692 nm,[41] and dipole moment of DL-α-amino butyric acid and DL-valine 16.0 D.[41]

shown in Table 1. It is true that salt solubilities of DL-α-Aba and DL-valine are effectively supervised by temperature and a number of physiochemical characteristics. In the analysis presented here, we assessed the solubility of mentioned amino acid (DL-α-Aba and DL-valine) in a water–Na_2SO_4 solvent system in between five evenly spaced temperatures range (288.15–308.15 K). The variations of solubilities in aqueous Na_2SO_4 solutions at different temperatures are shown in Figs. 1*a* and 1*b*. From all these experimental data, the following observations are found:

a) The solubilities of DL-α-Aba and DL-valine in water–Na_2SO_4 system rise with enhancement of temperature for a fixed tabular concentration value (Table 1).
b) The solubility of DL-α-Aba and DL-valine in water–Na_2SO_4 system reduces with increasing concentration at any particular tabulated temperature value (Figs. 1*a* and 1*b*).

Solvent water molecules are associated through intermolecular H-bonding. When temperature rises up, those interconnections become weak due to hike in kinetic energy of solvent molecules that in turn produce better solvent–solute interactions due to enrichment of more and more free water molecules resulting in solubility enhancement.

In aqueous media, the solubilities of DL-α-Aba and DL-valine due to ion–dipole interaction exist between carboxyl and amine ions of the solutes and dipolar water. However, compared to both amino acids molecules, polar water interacts with the ions of the corresponding electrolytes in a superior way rather than with the non-polar hydrocarbon part in both amino acid's moiety. Consequently, solubility of both amino acids diminishes in aqueous Na_2SO_4 solutions compared to non-electrolytic water solution (Fig. 2). Greater proportionate of hydrocarbon part in any amino acid moiety, lower its solubility and this helps to conclude that DL-valine shows lower solubility than other mentioned amino acid at any particular tabulated concentration value.

Another significant factor in electrolyte solvent system is salting-in/salting-out effect that might be producing profound influence on the solubility behavior of the protein building unit in electrolytic binary or ternary solutions. The salting-out constant can be determined with the help of the following equation:

$$\log(Ss/S_R) = K_{si}C \quad (15)$$

where K_{si} is salting-out constant; S_s and S_R are the solubility of present amino acids in electrolyte solution and reference solvent (H_2O), respectively; C is the molarity of electrolyte solution.

We have calculated the relative solubility data (Table 6) for better understanding the experimental variation of solubility in aqueous electrolyte solvent system. We can assess the importance of K_{si} using a plot of log (S_s/S_R) versus C (Fig. 3). The precise value of the constant K_{si} for the amino acids is given by the slope of the linear connection of the plot of log (S_s/S_R) versus C (Fig. 3). The experimental solubility and the calculated K_{si} values are in excellent agreement. Negative value of K_{si} concludes salting-out, while its positive value indicates salting-in. In the present solvent system, the value of K_{si} is negative (−0.1983) (standard deviation: ±0.0179) for DL-α-Aba and it was found the value is −0.1989 (standard deviation: ±0.0066) for DL-valine, which support strong salting-out effect, which in turn indicates that the solubility of both amino acids decreases in aqueous solution in the presence of sodium sulfate electrolyte.

4.2. Transfer Gibbs free energetics

Figure 4 and Tables 3 and 5 reveal the $\Delta G_t^0(i)$ for DL-α-Aba and DL-valine in earlier mentioned solvent system. The following observations are found:

a) The Gibbs free energy in total for transfer ($\Delta G_t^0(i)$) value increases with rise of concentration of electrolyte (Fig. 4).

Fig. 1. (*a*) Solubility of DL-α-amino acid (Aba) in different concentrations of Na_2SO_4 in aqueous-Na_2SO_4 solvent system with the variation of temperatures. (*b*) Solubility variation of DL-valine in different molarity of Na_2SO_4 with the variation of temperatures.

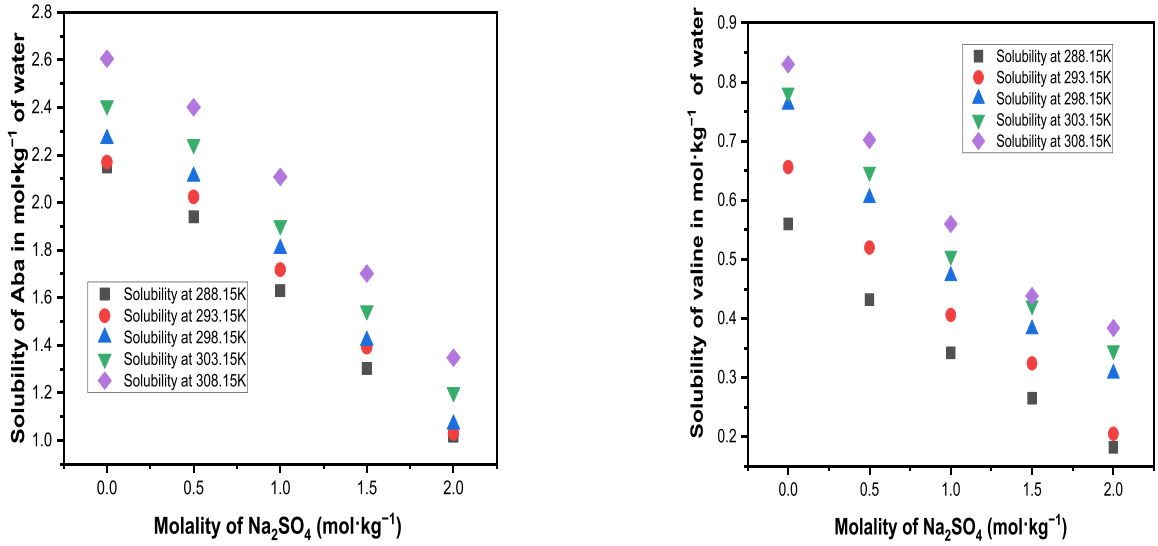
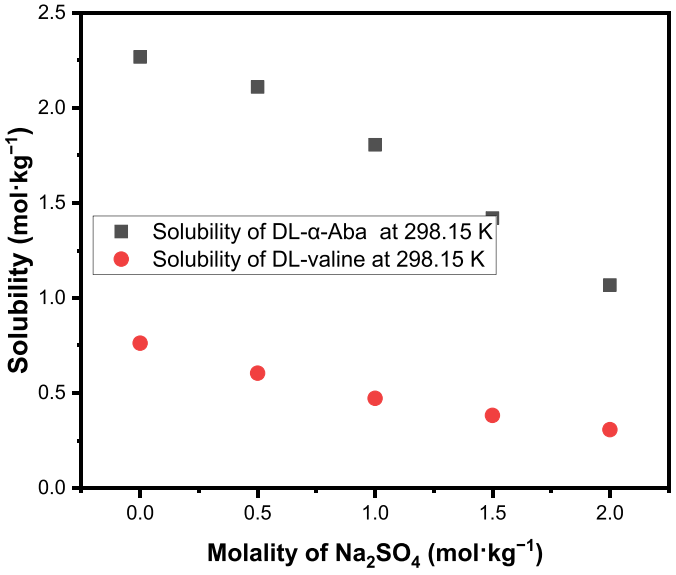


Fig. 2. Solubility variations of DL-α-Aba and DL-valine in aqueous electrolyte (Na_2SO_4) mixtures in different molarity at standard temperature 298.15 K.



b) The Gibbs free energy transfer for chemical interactions ($\Delta G^0_{t,\mathrm{ch}}(i)$) value steps up with rise of concentration of electrolyte (Fig. 4).

The variation of ($\Delta G^0_t(i)$) largely depends on dipole–dipole interaction ($\Delta G^0_{t,d-d}(i)$), cavity construction energy ($\Delta G^0_{t,\mathrm{cav}}(i)$), and free energy for different non-covalent chemical interactions ($\Delta G^0_{t,\mathrm{ch}}(i)$) such as aquaphobic, aquaholics, acid–base, and dispersion in a combined and chronological way. The idea of solute–solvent interlinking in electrolyte media may be used to partially explain the reasons for the interpretations.

In this study, we calculate these values with the help of least square method by calculating coefficients *a*, *b*, and *c* (Table 3). In Na_2SO_4 solvent system, positive increment of ($\Delta G^0_t(i)$) value is observed because of lowering propensity of forming complex with electrolyte. This is in turn may be due to the presence of hydrocarbon part in the solute amino acid molecules. This hydrocarbon part resists making interactions with the sodium and sulfate ions present in the solution. Subsequently, with rise of sodium sulfate concentration $\Delta G^0_t(i)$ shows positive increment. While cavity construction and dipole–dipole associations are crucial factors contributing to the stability of amino acids in solution, their interactions in solvation processes, particularly the total transferrable Gibbs free energy ($\Delta G^0_t(i)$), enhances the ($\Delta G^0_{t,\mathrm{ch}}(i)$) value in a favorable measure. Therefore, these chemical interactions lead to the instability of the solutes amino acids in electrolytic solution with the increased concentration of Na_2SO_4 in Na_2SO_4–water solvent system.

However, the chemical transfer free energy change for both amino acids ($\Delta G^0_{t,\mathrm{ch}}(i)$) is majorly controlled by several solvent–solute chemical interactions in the presence of electrolytes. This function makes up of a variety of type of interconnections exhibiting between solute molecules chemically and solvent like H-bonding, dispersion, hydrophobic interaction, etc. This term can be evaluated accurately by subtracting cavity forming ($\Delta G^0_{t,\mathrm{cav}}(i)$) and dipole–dipole energy ($\Delta G^0_{t,d-d}(i)$). All corresponding energy values are shown collectively in Table 5. Figure 5 shows the increasing nature of variation of chemical transfer Gibbs free energies for the amino acids in aqueous sodium sulfate solution. This clearly

Table 6. Relative solubility (S_S/S_R) and log (S_S/S_R) of DL-α-amino butyric acid and DL-valine in water and water + Na_2SO_4 in different compositions of Na_2SO_4 at different temperatures under atmospheric pressure, $p = 0.1$ MPa[a].

Molality (mol kg^{-1})	Relative solubility in (mol kg^{-1})									
	Relative solubility (S_S/S_R) 288.15 K	Log (S_S/S_R) at 288.15 K	Relative solubility (S_S/S_R) 293.15 K	Log (S_S/S_R) at 293.15 K	Relative solubility (S_S/S_R) 298.15 K	Log (S_S/S_R) at 298.15 K	Relative solubility (S_S/S_R) 303.15 K	Log (S_S/S_R) at 303.15 K	Relative solubility (S_S/S_R) 308.15 K	Log (S_S/S_R) at 308.15 K
DL-α-amino butyric acid in water + Na_2SO_4 (m)										
0.5	0.9023	−0.0446	0.9327	−0.0303	0.9303	−0.0314	0.9323	−0.0304	0.9216	−0.0355
1.0	0.7581	−0.1203	0.7917	−0.1014	0.7963	−0.0989	0.8754	−0.0577	0.8092	−0.0919
1.5	0.6056	−0.2178	0.6415	−0.1928	0.6261	−0.2034	0.6420	−0.1925	0.6534	−0.1848
2.0	0.4335	−0.3630	0.4747	−0.3236	0.4709	−0.3271	0.4991	−0.3018	0.5175	−0.2861
DL-valine in water + Na_2SO_4 (m)										
0.5	0.7714	−0.1127	0.7927	−0.1009	0.7926	−0.1008	0.8286	−0.0816	0.8458	−0.0727
1.0	0.6107	−0.2142	0.6189	−0.1618	0.6194	−0.1875	0.6471	−0.1890	0.6746	−0.1709
1.5	0.4732	−0.3249	0.4939	−0.3064	0.5013	−0.2999	0.5396	−0.2679	0.5277	−0.2776
2.0	0.3250	−0.4881	0.3125	−0.5051	0.4029	−0.3948	0.4425	−0.3541	0.4627	−0.3347

Fig. 3. Plot of log (S_S/S_R) versus molality of electrolyte (mol kg^{-1}) in different compositions of electrolyte at 298.15 K.

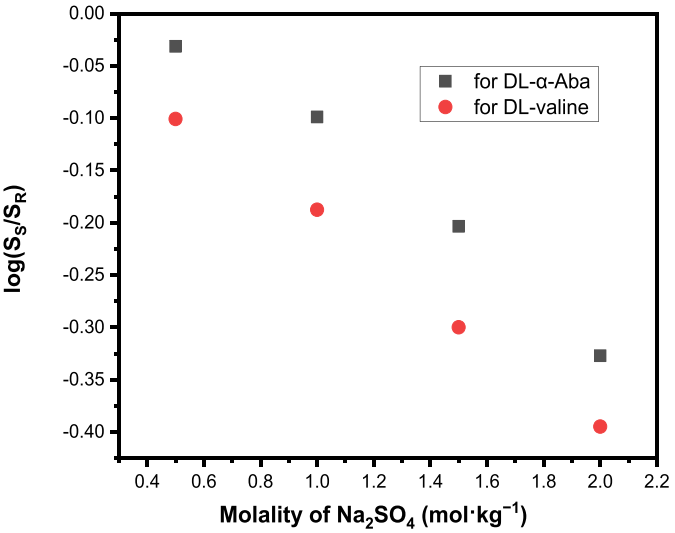
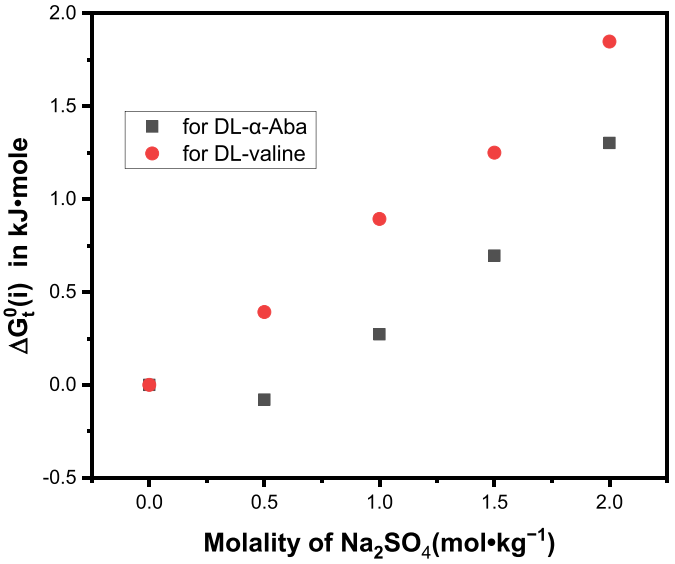


Fig. 4. Variation of ΔG_t^0 (i) for DL-α-Aba and for DL-valine in Na_2SO_4–H_2O solution in different compositions at 298.15 K.



indicates that the destabilization of DL-valine is more than DL-α-Aba in Na_2SO_4–water solvent system due to greater percentage of hydrocarbon part in former amino acid moiety.

4.3. Transfer entropies

Solvent–solvent interaction contributes major hands behind the appearing of total transfer entropies. Figure 6 and Table 5 address the relevant experimental results. The experimental data are further calculating with the help of least square approach to find out more precise goal. Figure 6 excellently reveals that $T\Delta S_t^0$ (i) rises up with concentration of electrolyte. $T\Delta S_t^0$ (i) is defined as the sum of interactional result of cavity construction transfer entropy ($T\Delta S_{t,cav}^0$ (i)) and transfer entropy resulting from dipole–dipole inter-association

Fig. 5. Plot of $\Delta G^0_{t,ch}(i)$ for DL-α-Aba and for DL-valine in Na_2SO_4 solution in different composition at 298.15 K.

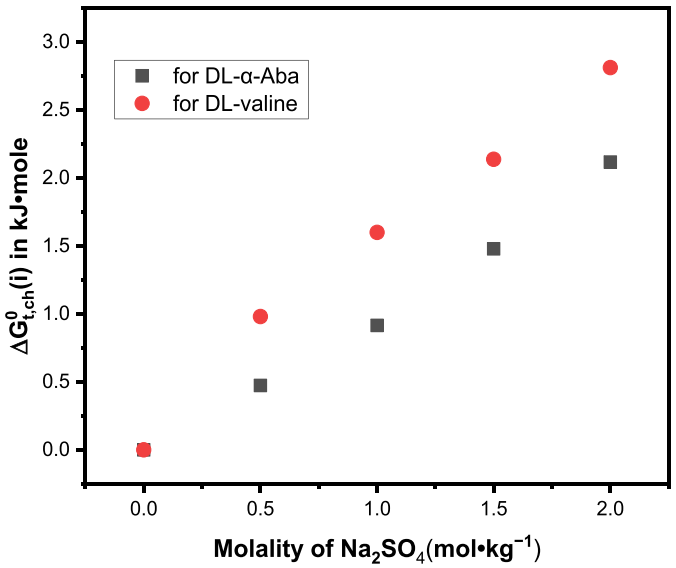
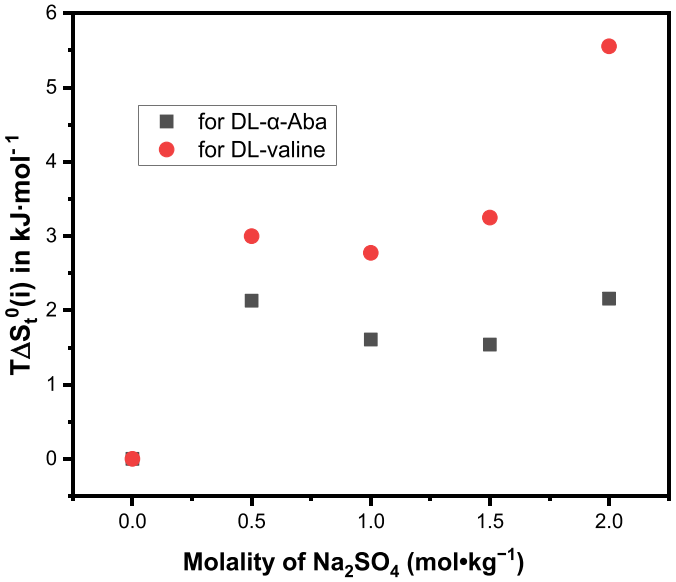


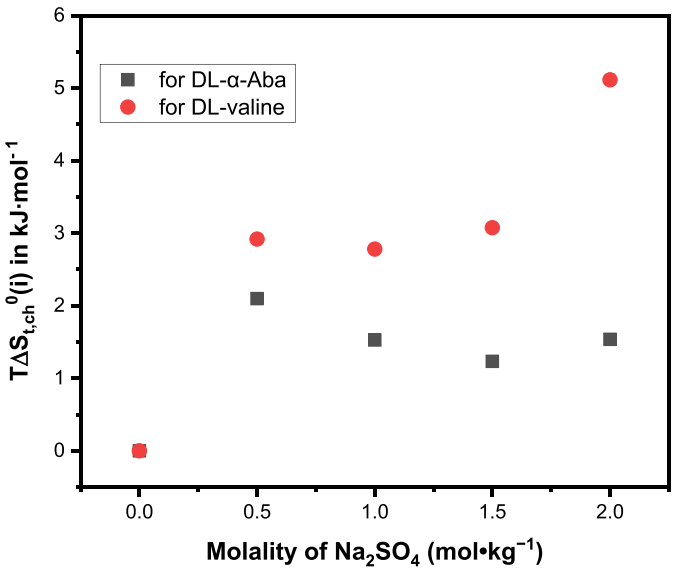
Fig. 6. Plot of $T\Delta S^0_t(i)$ for DL-α-Aba and for DL-valine in Na_2SO_4–H_2O solution in different electrolytic concentrations at 298.15 K.



$T\Delta S^0_{t,d-d}(i)$ and $T\Delta S^0_{t,ch}(i)$, which are also associated with some weak interactional parameters, namely hydrophobic, acid-base, H-bonding, etc.

It is examined that $T\Delta S^0_{t,ch}(i)$ for both amino acids attain more positive values (more disordered) in Na_2SO_4–H_2O system rather than in pure water (Fig. 7). This fact also supported by decreasing trend on solubility of the amino acids with increasing electrolyte concentration at a particular temperature, resulting more solvent molecules become free and hence both entropies factors increases in positive direction. The tabulated inspection also suggests that DL-α-Aba induce

Fig. 7. Plot of $T\Delta S^0_{t,ch}(i)$ values for DL-α-Aba and for DL-valine in Na_2SO_4–H_2O solution in different composition at 298.15 K.



less solvent–solvent interaction compared to DL-valine in Na_2SO_4 and H_2O. Since Na^+ is tiny and strongly solvated by water molecules due to its small size, the notion of hydration may be used to explain why some values are more disordered than others. Thus, DL-α-Aba interacts more strongly with H_2O present in Na_2SO_4–H_2O system and therefore, it enhances more orderings compared to DL-valine that interacts less with the solvent molecules resulting positive increment $T\Delta S^0_{t,ch}(i)$ values in Na_2SO_4–H_2O system.

5. Conclusion

In this current work, the solvation properties and connected solvation parameters of DL-α-Aba and DL-valine were assessed in an aqueous-Na2SO4 solvent system at five temperatures and tabulated in Table 1. The experimental measured variations basically explained on the ground of size, salting-in/out constant, and hydrocarbon part. Several interactions like dipole–dipole, dispersion, H-bonding, etc. are influencing many properties in a large extent in this study. At any particular tabulated temperature value, the solubility of both concerned amino acids decreases with rising of electrolyte concentration owing to salting-out phenomenon. Nonetheless, with temperature enhancement the solubility of both experimental amino acids moves to higher value gradually indicating their solubility enhancement due to increasing a greater number of free water molecules for crumbling of H-bonding present in between solvent water molecules. The hydrocarbon part is mainly responsible for the difference of solubility showing by those amino acids under a particular experimental condition. Solvent–solute and solvent–solvent interactions in electrolytic environment are the controlling factors for showing variations for chemical transfer Gibbs energy ($\Delta G^0_{t,ch}(i)$) and chemical transfer entropy ($T\Delta S^0_{t,ch}(i)$), respectively. The outcome suggests that the larger amino

acid DL-valine is less soluble than DL-α-amino butyric acid in aqueous-Na_2SO_4. This research also concludes that the solubility of the solutes in aqua-Na_2SO_4 system rises with enhancement of temperature for a particular concentration value and amino acids feel more comfortable stability in pure H_2O system rather than Na_2SO_4–water system, which are supported by the solubility data and other related solvation thermodynamics parameters. Additionally, the findings of the current investigation are crucial not only in the broad field of amino acid research, but also in the medical and industrial sectors.

Acknowledgement

Dr. Roy acknowledged Netaji Subhas Open University for financial assistant to complete the project of the present research (Project office order Memo No.: AC/140/2021-22 dated 1 November 2021 and Project No. Reg/1290 dated 22 November 2021). The authors acknowledge the financial support from the Strategic Academic Leadership Program of the Southern Federal University ("Priority 2030").

Article information

History dates

Received: 29 October 2023
Accepted: 27 February 2024
Accepted manuscript online: 18 March 2024
Version of record online: 7 May 2024

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Data availability

All data generated or analyzed during this study are given in full within this article.

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Validation: SR
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Competing interests

The authors have no competing interests.

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