

Experimental Measurement and Correlation of two α -Amino Acids Solubility in Aqueous Salts Solutions from 298.15 to 323.15 K

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Abstract – By the gravimetric method at atmospheric pressure, the solubility of two α -amino acids was resolved over temperatures from (293.15 to 323.15) K. The α -amino acids studied were L-arginine and L-histidine. Results showed a salting-out effect on the solubility of the tested amino compounds. It is obvious that there was an increase in the solubility, in aqueous chloride solutions, with the increasing temperature. Results were translated regarding the salt hydration shells and the ability of the solute to form hydrogen-bond with water. The solubility data was precisely associated with a semi-empirical equation. The standard molar Gibbs free energies of transfer of selected α -amino compounds ($\Delta_{tr}G^\circ$) from pure water to aqueous solutions of the chloride salts have been calculated from the solubility data. The decrease in solubility is correlated to the positive ($\Delta_{tr}G^\circ$) value which is most part of the enthalpic origin.

Key words: L-histidine, L-arginine, Chloride salt effect, Solubility-temperature dependence, Transfer Gibbs free energies

1. Introduction

Amino acids are of importance due to their applications in pharmaceuticals, cosmetics, food industries and fine chemicals [1-6]. Solubility behavior of biomolecules and thermodynamic properties is an important physicochemical parameter useful in separation and purification method from solution. Many factors affect the solubility such as experimental temperature [7], ionic strength [8], acidity or alkalinity of the media [9,10] chemical structure, the polarity of the solvents [11], and the concentration of the electrolyte present in aqueous solution [12], hence, the thermodynamics of solvation significantly.

Previous studies demonstrated that the presence of an electrolyte (NaCl, KCl, KNO₃ etc.) causes a variation in actual orientation of amino acids and the solubility properties [13-17]. To comprehend the addition impact of electrolytes on the thermodynamic properties, the investigation of thermodynamic parameters of transfer is especially fundamental. It is an interesting role in light of the fact that studies give profitable data with respect to the protein folding and unfolding process [18,19] and the degree of hydrophobic association of amino acid.

This paper is a continuation of our previous paper studying the solubility-temperature dependence data for L-glutamic acid [20], in aqueous solutions of various concentrations of (NaCl and KCl). The solubility temperature dependence data for two α -amino acids was

reported: L-arginine ((S)-2-Amino-5-guanidinopentanoic acid) and L-histidine ((S)-2-Amino-3-(4-imidazolyl)propionic acid. Chloride salt aqueous solutions were used to carry out this study. The information acquired for every chloride salt (NaCl and KCl) concentration was utilized to ascertain appropriate thermodynamic properties, for example, free energy ($\Delta_{sol}G^\circ$), molar enthalpy of dissolution ($\Delta_{sol}H^\circ$), and molar entropy of dissolution ($\Delta_{sol}S^\circ$), which have practical importance for industrial optimization processes.

2. Materials and Methods

2-1. Chemicals

Amino acids L-arginine (CAS: 74-79-3, C₆H₁₄N₄O₂, MW = 174.20 g·mol⁻¹, $\geq 98\%$ purity) and L-histidine (CAS: 71-00-1, C₆H₉N₃O₂, MW = 155.15 g·mol⁻¹, $\geq 99\%$ purity), were obtained from Acros Organics and used without further purification (Scheme 1). Potassium chloride (CAS: 7440-09-7, MW = 74.56 g·mol⁻¹) and sodium chloride (CAS: 7647-14-5, MW = 58.44 g·mol⁻¹) (all $>99\%$ purity) were bought from Sigma-Aldrich (Germany). Purified water was prepared from Elga Purelab purification (Maxima Ultra Pure Water, Elga-Prima Corp, UK).

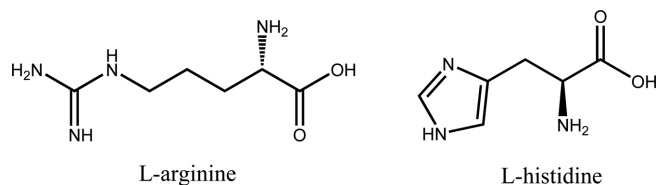
2-2. Measurement of α -amino Acids solubility

The apparatus, experimental procedures, preparation of the aqueous solutions of chloride (NaCl and KCl) and method for α -amino acids solubility estimations are to a great extent depicted in past publications [20-24]. Two autonomous trials were acknowledged to decide the amino acid solubility by using a thermostatted reactor and a simple gravimetric method at atmospheric pressure. Information about the

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Scheme 1. Molecular structure of L-arginine and L-histidine.

reproducibility of the technique is shown in the past referenced papers [20-24].

3. Experimental Results and Discussion

All results from some previous literature on measured solubility study of α -amino acids in water at different temperatures are regrouped in Table 1 [25-27] and shown in Fig. 1. From Fig. 1, the deviations between reference [25,26] and our results are relatively small for L-arginine and L-histidine. It was demonstrated that this exploratory strategy was dependable. The solubility of L-arginine in water that was reported by Hayashi *et al.* 1966 [27] is higher than the solubility measured for this work.

In a previous publication [20], the effect on the solubility of L-glutamic acid of the additional data of chloride salt at the temperature ranging from 298.15 to 323.15 K was reported. Here, a similar report

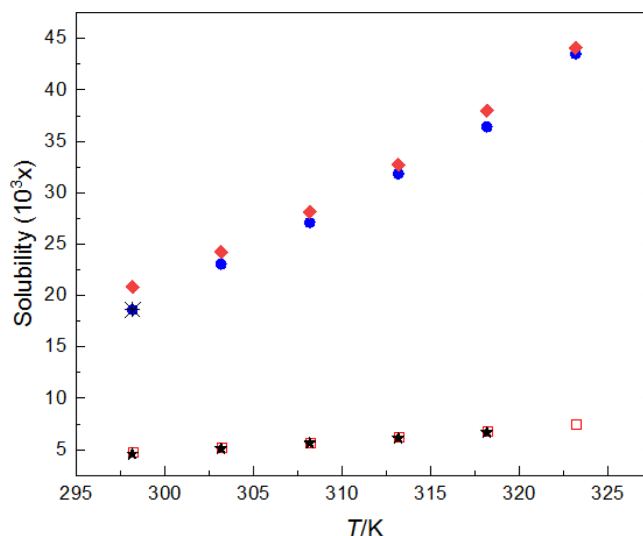


Fig. 1. Mole fraction solubility (x) of L-arginine and L-histidine in water in this work compared to literature: For L-histidine, ★, Liu *et al.*, 2017; □, this work and for L-arginine, ♦, Hayashi *et al.*, 1966; *, Liu *et al.*, 2017; ●, this work.

proceeded for two α -amino acids (L-arginine and L-histidine) utilizing a similar chloride salts, i.e., NaCl, and KCl at various molality. Tables 2 and 3 show the experimental data collected in this work. Strikingly, at various concentrations α -amino acids have a higher solubility within

Table 1. Mole fraction solubility of L-arginine and L-histidine in water at different temperature and under atmospheric pressure, $p = 101.3$ kPa in the present study and in literature

T/K	L-arginine			T/K	L-histidine	
	$10^3 x_{\text{exptl}}^a$	$10^3 x_{\text{lit}}^b$ [25]	$10^3 x_{\text{lit}}^b$ [26]		$10^3 x_{\text{exptl}}$	$10^3 x_{\text{lit}}^b$ [27]
298.15	18.616	18.614	20.813	298.15	4.769	4.587
303.15	23.039		24.215	303.15	5.188	5.100
308.15	27.097		28.156	308.15	5.714	5.621
313.15	31.833		32.717	313.15	6.253	6.131
318.15	36.408		37.989	318.15	6.785	6.674
323.15	43.510		44.071	323.15	7.535	

^a x_{exptl} is the experimentally determined solubility of L-arginine and L-histidine. Standard uncertainty u is $u(T) = 0.01$ K. The relative standard uncertainty u is $u_r(p) = 0.05$, $u_r(x_{\text{exptl}}) = 0.02$ and $u_r(p) = 0.05$. ^bData from literature.²⁹

Table 2. Molal solubilities ($\text{mol} \cdot \text{kg}^{-1}$) of L-arginine in aqueous NaCl and KCl solutions in different compositions of chloride salts, over the temperature range from 298.15 to 323.15 K at $p = 101.3$ kPa^a

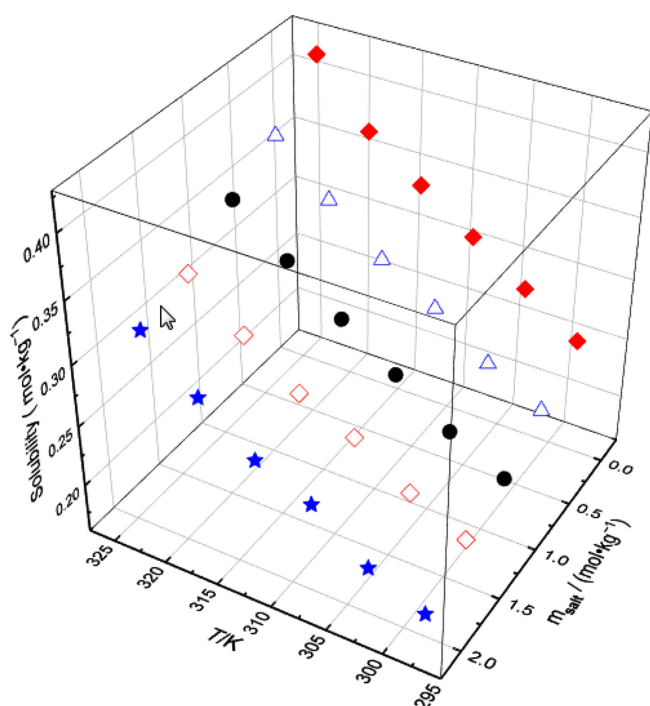
T/K		NaCl	KCl	T/K	NaCl	KCl
L-arginine	Salt-H ₂ O molality (m)	0.50		1.00		
	298.15	1.0147	1.0426	298.15	0.9520	1.0023
	303.15	1.1778	1.2175	303.15	1.1008	1.1542
	308.15	1.3019	1.3900	308.15	1.2309	1.3014
	313.15	1.4498	1.5732	313.15	1.3710	1.4794
	318.15	1.6335	1.7635	318.15	1.5474	1.6883
	323.15	1.8612	1.9834	323.15	1.7168	1.8835
	Salt-H ₂ O molality (m)	1.50		2.00		
	298.15	0.9028	0.9680	298.15	0.8176	0.8601
	303.15	1.0261	1.1090	303.15	0.9124	0.9790
	308.15	1.1607	1.2395	308.15	1.0291	1.1038
	313.15	1.3022	1.3928	313.15	1.1452	1.2423
	318.15	1.4426	1.6157	318.15	1.2902	1.4002
	323.15	1.6147	1.7653	323.15	1.4512	1.5641

^aStandard uncertainties u are $u(T) = 0.01$ K and $u(m) = 0.01 \text{ mol} \cdot \text{kg}^{-1}$; relative uncertainties, and $u_r(S_{\text{Glu}}) = 0.02$ and $u_r(p) = 0.05$.

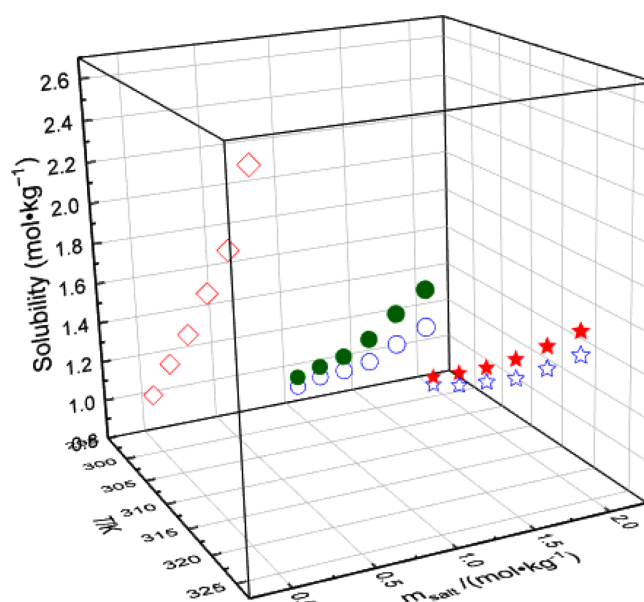
Table 3. Molal solubilities ($\text{mol}\cdot\text{kg}^{-1}$) of L-histidine in aqueous NaCl and KCl solutions in different compositions of chloride salts, over the temperature range from 298.15 to 323.15 K at $p = 101.3 \text{ kPa}^a$

	T/K		NaCl		KCl	
	Salt-H ₂ O molality (m)		0.50		1.00	
L-histidine	298.15		0.2321		0.2394	
	303.15		0.2559		0.2678	
	308.15		0.2868		0.2965	
	313.15		0.3125		0.3323	
	318.15		0.3468		0.3591	
	323.15		0.3847		0.3995	
	Salt-H ₂ O molality (m)		1.50		2.00	
	298.15		0.1998		0.2161	
	303.15		0.2212		0.2429	
	308.15		0.2504		0.2681	
	313.15		0.2703		0.3050	
	318.15		0.3016		0.3301	
	323.15		0.3355		0.3646	

^aStandard uncertainties u are $u(T) = 0.01 \text{ K}$ and $u(m) = 0.01 \text{ mol}\cdot\text{kg}^{-1}$; relative uncertainties, and $u_r(S_{\text{Glu}}) = 0.02$ and $u_r(p) = 0.05$.

**Fig. 2.** Solubility of L-histidine in aqueous NaCl solutions at various temperatures: $\blacklozenge$, in pure water; $\blacktriangle$, $0.5 \text{ mol}\cdot\text{kg}^{-1}$ NaCl; $\bullet$, $1 \text{ mol}\cdot\text{kg}^{-1}$ NaCl; $\square$, $1.5 \text{ mol}\cdot\text{kg}^{-1}$ NaCl, $\star$, $2 \text{ mol}\cdot\text{kg}^{-1}$ NaCl.

the sight of potassium than within the sight of sodium when chloride is the anion. The impacts of chloride on the solvency of L-arginine are outlined in Fig. 2. The outcome demonstrated a decline in the solubility of α -amino acids within the sight of an expanding measure of chloride salts (salting-out impact). The applied model for this salting-out impact identifies with the solid inclination of ionic solutes to form shells of firmly bound water (hydration shells). Thus, as the concentration of the chloride salts increases, more water is bound up in hydration shells, and in this way the solubility. From Tables 2 and 3 it is very well known that all the concentrated amino acids demonstrate a solubility increment with increasing temperature.

**Fig. 3.** Solubility of L-arginine in pure water and in various chloride solutions versus temperature T . $\blacklozenge$, in pure water; $\bullet$, $1 \text{ mol}\cdot\text{kg}^{-1}$ KCl; $\circ$, $1 \text{ mol}\cdot\text{kg}^{-1}$ NaCl; $\star$, $2 \text{ mol}\cdot\text{kg}^{-1}$ KCl, $\star$, $2 \text{ mol}\cdot\text{kg}^{-1}$ NaCl.

In the temperature range studied, it is very well noticed that all the concentrated amino acids demonstrated a solubility increment with the increasing temperature. The L-histidine solubility was introduced as a component of temperature in pure water and within the sight of various molalities of chloride salt (Fig. 2). The solubility of L-arginine in purified water and in different chloride solutions as an arrangement as an element of temperature is exhibited in Fig. 3. The outcomes in Fig. 3 approved the salting-out request got at $T = 298.15 \text{ K}$. This can be credited to the more articulated solvation level of Na^+ by water molecules when compared to K^+ [28-30], which diminishes the degrees of freedom of the water particles and thus prompts a solute solubility decline within the presence of salts when compared with that in unadulterated water.

3-1. Temperature effect in aqueous chloride solutions

The solubility-temperature reliance of examined dependence of studied α -amino acids in aqueous chloride solutions was fitted to the empirical equation proposed by Heidman *et al.* [31].

$$\ln x = A + \frac{B}{T} + C \ln(T) \quad (1)$$

Obviously, x is the mole fraction solubility of amino acid at temperature T (K), and A , B , and C are empirically-derived constants. The estimations of A and B stand for the variety in the solution activity coefficient, and the C value reflects the impact of temperature on the fusion enthalpy [32].

The computed values of the solubility of amino acids in various

chloride aqueous solutions from $T = 293.15$ to 323.15 K at pressure $p = 101.3$ kPa is also listed in Tables 4 and 5 and visually in Figs. 4 and 5. It may be discovered that the contrasts between the determined information and test data are little inside the experimental temperature range.

The parameters of the modified empirical equation and the root mean-square deviations (RMSD) are also listed in Table 6. The RMSD can be calculated by Eq. 2.

$$\text{RMSD} = \left[\frac{1}{n} \times \sum_{i=1}^n (x_{\text{calcd}} - x_{\text{exptl}})^2 \right]^{1/2} \quad (2)$$

in which n is the total number of experimental data points, which are 6 in this work; x_{calcd} and x_{exptl} represent the computed and the

Table 4. Experimental and correlated mole fraction solubility of L-arginine in different molalities of aqueous chloride solutions at temperatures ranging from 298.15 to 323.15 under $p = 101.3$ kPa^a

Salt	NaCl		KCl		NaCl		KCl		
Salt molality (m)	0.50				1.00				
T/K	$10^3 \cdot x_{explt}^b$	$10^3 \cdot x_{calcd}^b$	$10^3 \cdot x_{explt}$	$10^3 \cdot x_{calcd}$	T/K	$10^3 \cdot x_{explt}$	$10^3 \cdot x_{calcd}$	$10^3 \cdot x_{explt}$	$10^3 \cdot x_{calcd}$
298.15	18.316	18.5352	18.9625	19.2939	298.15	17.558	17.7706	18.7785	18.905
303.15	21.197	20.820	22.0727	21.9106	303.15	20.248	19.9920	21.5641	21.462
308.15	23.378	23.342	25.1228	24.8304	308.15	22.586	22.448	24.2467	24.315
313.15	25.964	26.122	28.3391	28.0828	313.15	25.093	25.158	27.4721	27.491
318.15	29.158	29.181	31.6592	31.699	318.15	28.230	28.145	31.2308	31.022
323.15	33.089	32.541	35.4662	35.714	323.15	31.225	31.432	34.7166	34.941
Salt molality (m)	1.50				2.00				
T /K	$10^3 \cdot x_{explt}$	$10^3 \cdot x_{calcd}$	$10^3 \cdot x_{explt}$	$10^3 \cdot x_{calcd}$	T /K	$10^3 \cdot x_{explt}$	$10^3 \cdot x_{calcd}$	$10^3 \cdot x_{explt}$	$10^3 \cdot x_{calcd}$
298.15	17.019	17.1420	18.6985	18.817	298.15	15.771	15.6879	17.1707	17.249
303.15	19.298	19.2828	21.3642	21.262	303.15	17.568	17.6197	19.4976	19.455
308.15	21.773	21.649	23.8179	23.977	308.15	19.770	19.7518	21.9279	21.900
313.15	24.365	24.261	26.6844	26.987	313.15	21.952	22.101	24.6133	24.605
318.15	26.920	27.139	30.8239	30.318	318.15	24.662	24.686	27.6550	27.594
323.15	30.036	30.305	33.5821	33.998	323.15	27.655	27.526	30.7923	30.890

^aStandard uncertainty u is $u(T) = 0.01$ K. The relative standard uncertainty u is $u_r(p) = 0.05$, $u_r(x_{\text{exptl}}) = 0.02$. ^b x_{exptl} is the experimentally determined solubility of L-arginine; x_{calcd} is the calculated solubility of L-arginine by the modified empirical equation (2).

Table 5. Experimental and correlated mole fraction solubility of L-histidine in different molalities of aqueous chloride solutions at temperatures ranging from (298.15 to 323.15 under $p = 101.3$ kPa^a

Salt		NaCl		KCl		NaCl		KCl	
Salt molality (m)		0.50				1.00			
T/K	$10^3 \cdot x_{\text{explt}}^b$	$10^3 \cdot x_{\text{calcd}}^b$	$10^3 \cdot x_{\text{explt}}$	$10^3 \cdot x_{\text{calcd}}$	T/K	$10^3 \cdot x_{\text{explt}}$	$10^3 \cdot x_{\text{calcd}}$	$10^3 \cdot x_{\text{explt}}$	$10^3 \cdot x_{\text{calcd}}$
298.15	4.250	4.244	4.4195	4.440	298.15	3.954	3.948	4.2865	4.333
303.15	4.684	4.703	4.9394	4.925	303.15	4.384	4.418	4.8466	4.822
308.15	5.245	5.202	5.4661	5.453	308.15	4.967	4.935	5.4132	5.356
313.15	5.713	5.745	6.1225	6.028	313.15	5.530	5.503	6.0493	5.940
318.15	6.336	6.335	6.6126	6.653	318.15	6.132	6.126	6.5045	6.576
323.15	7.024	6.975	7.3512	7.332	323.15	6.768	6.807	7.2811	7.269
Salt molality (m)		1.50				2.00			
T/K	$10^3 \cdot x_{\text{explt}}$	$10^3 \cdot x_{\text{calcd}}$	$10^3 \cdot x_{\text{explt}}$	$10^3 \cdot x_{\text{calcd}}$	T/K	$10^3 \cdot x_{\text{explt}}$	$10^3 \cdot x_{\text{calcd}}$	$10^3 \cdot x_{\text{explt}}$	$10^3 \cdot x_{\text{calcd}}$
298.15	3.817	3.824	4.2367	4.257	298.15			4.1962	4.216
303.15	4.224	4.253	4.7588	4.736	303.15			4.7071	4.687
308.15	4.780	4.721	5.2498	5.261	308.15			5.1922	5.201
313.15	5.157	5.232	5.9688	5.834	313.15			5.9029	5.761
318.15	5.751	5.789	6.4555	6.459	318.15			6.3350	6.372
323.15	6.392	6.396	7.1254	7.139	323.15			7.0615	7.036

^aStandard uncertainty u is $u(T) = 0.01$ K. The relative standard uncertainty u is $u_r(p) = 0.05$, $u_r(x_{\text{exptl}}) = 0.02$. ^b x_{exptl} is the experimentally determined solubility of L-arginine; x_{calcd} is the calculated solubility of L-arginine by the modified empirical equation (2).

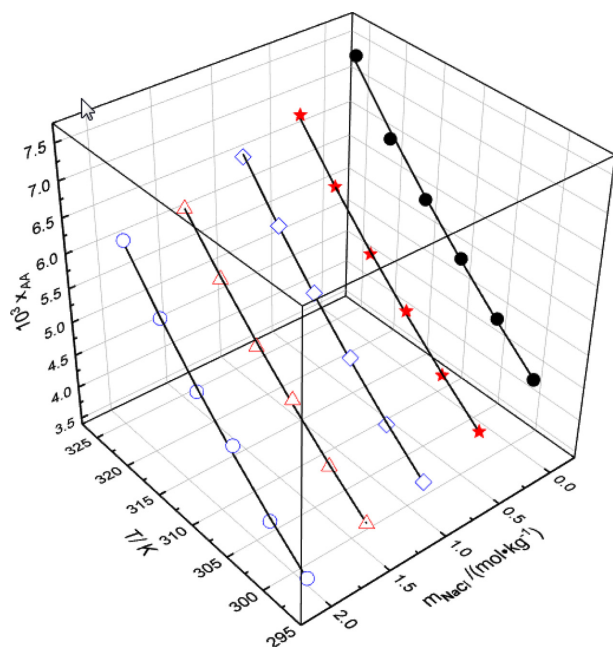


Fig. 4. Experimental and correlated solubility of L-histidine in various NaCl aqueous solutions. Symbols are for experimental points and lines for correlated data with Eq. 2: ●, pure water; ★, 0.5 mol·kg⁻¹; ◆, 1.0 mol·kg⁻¹; ▲, 1.5 mol·kg⁻¹; ○, 2.0 mol·kg⁻¹.

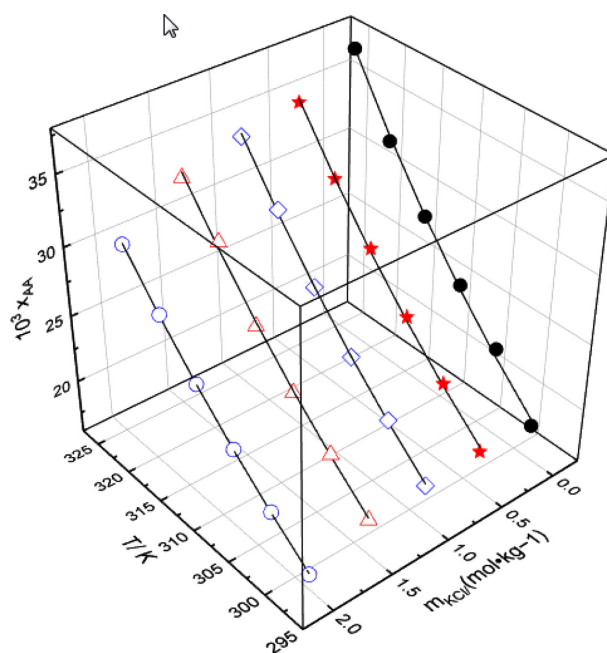


Fig. 5. Experimental and correlated solubility of L-arginine in various KCl aqueous solutions. Symbols are for experimental points and lines for correlated data with Eq. 2: ●, pure water; ★, 0.5 mol·kg⁻¹; ◆, 1.0 mol·kg⁻¹; ▲, 1.5 mol·kg⁻¹; ○, 2.0 mol·kg⁻¹.

Table 6. Optimized parameters, RAD and RMSD of Eq. (2) for selected amino acid in different aqueous chloride solutions

	A^a	B^a	C^a	10^4RMSD^b	10^2RAD^c
L-arginine	Salt molality (m)	0.00			
		-62.476	0.073	10.270	1.289
	Salt molality (m)	0.50			
	NaCl	-43.825	0.492	6.992	0.831
	KCl	-47.529	0.448	7.649	0.999
	Salt molality (m)	1.00			
	NaCl	-44.393	0.484	7.084	0.673
	KCl	-47.443	0.458	7.630	0.307
	Salt molality (m)	1.50			
	NaCl	-44.395	0.484	7.078	0.240
	KCl	-45.843	0.493	7.348	0.922
	Salt molality (m)	2.00			
L-histidine	NaCl	-43.950	0.522	6.984	0.177
	KCl	-45.301	0.505	7.238	0.078
	Salt molality (m)	0.00			
		-37.632	0.642	5.665	0.159
	Salt molality (m)	0.50			
	NaCl	-40.635	0.577	6.173	0.194
	KCl	-40.916	0.574	6.230	0.150
	Salt molality (m)	1.00			
	NaCl	-44.098	0.504	6.768	0.269
	KCl	-42.065	0.553	6.428	0.676
	Salt molality (m)	1.50			
	NaCl	-41.972	0.558	6.389	0.627
	KCl	-42.065	0.553	6.424	0.125
	Salt molality (m)	2.00			
	NaCl	-47.243	0.446	7.299	1.908
	KCl	-41.719	0.591	6.362	0.183

^a A , B and C are the parameters of the modified Apelblat equation.

^b RAD and ^c $RMSD$ are relative average deviations and root-mean-square deviations, respectively.

experimental values solubility, accordingly.

The relative average deviation (RAD) is employed to estimate the error calculated with empirical equation, which is described as Eq. 3. The calculated values are also presented in Table 5.

$$\text{RAD} = \frac{1}{n} \times \sum_{i=1}^n \left| \frac{X_{\text{exptl}} - X_{\text{calcd}}}{X_{\text{exptl}}} \right| \quad (3)$$

Table 6 shows that the values of RMSD and RAD are not greater than 1.289×10^{-4} and 1.423×10^{-2} for L-arginine, 1.908×10^{-4} and 1.105×10^{-2} for L-histidine, accordingly, indicating that the computed solubility of the empirical equation agrees well with the experimental data.

From Tables 3 to 6 and Figures 2 and 3, the following conclusions were drawn:

- The solubility of amino acid compounds in chloride aqueous solutions increases with temperature.
- The chloride has a salting-out impact on the solubility of selected α -amino acids; with rising amount of chloride in water, the mass of α -amino acids dissolved in water decreases.
- The experimental data of selected compounds were well correlated by the selected modified empirical equation.

3-2. Thermodynamic parameters of transfer

According to the literature, the molar solubility of the studied amino acid (AA) in pure water corresponds to some thermodynamic parameters utilizing temperature and salt together with the effect data. Principally, the standard molar Gibbs free energy ($\Delta_{tr}G_{AA}^o$) of conveying of selected amino from pure water to chloride salts aqueous solutions was calculated. The commitments of the enthalpic and entropic terms were assessed by computing the standard molar enthalpy of transfer (Gibbs–Helmholtz condition) and the standard molar entropy of transfer. These parameters reflect the modification of the solution properties because of the nearness of the solute at its interminable dilution state at a given temperature [33]. Take for instance that the activity coefficient of amino acid in the aqueous phase is equivalent to 1 [34,35]. The $\Delta_{tr}G_{AA}^o$ of one mole of AA, at consistent temperature and weight, from pure water to aqueous solutions of chloride salts, is

expressed by Eq. 4 [36]:

$$\Delta_{tr}G^o = -RT \ln \left(\frac{S_{AA, \text{salt}}}{S_{AA, W}} \right) \quad (4)$$

where R is the molar gas constant, T is the absolute temperature, $S_{AA, W}$ and $S_{AA, \text{salt}}$ refer to the solubility of amino acid in pure water and in aqueous chloride salts solution, respectively, at the distribution equilibrium. To understand the salting phenomenon in the dissolution process of amino acid, the $\Delta_{tr}H_{AA}^o$ and $\Delta_{tr}S_{AA}^o$ of transfer of one of amino acid (AA) mole from unadulterated water to chloride salts aqueous solutions need to be studied.

According to literature, the $\Delta_{tr}H_{AA}^o$ and $\Delta_{tr}S_{AA}^o$ of transfer can be obtained as follows:

$$\Delta_{tr}H_{Glu}^o = T^2 \left[\frac{\partial(\Delta_{tr}G_{AA}^o/T)}{\partial T} \right]_p \quad (5)$$

$$\Delta_{tr}S_{Glu}^o = \frac{\Delta_{tr}H_{AA}^o - \Delta_{tr}G_{AA}^o}{T} \quad (6)$$

The calculated results of $\Delta_{tr}G_{AA}^o$, $\Delta_{tr}H_{AA}^o$ and $\Delta_{tr}S_{AA}^o$ from a perfect-diluted solution in pure water to an ideal-diluted solution in chloride salts ($1 \text{ mol} \cdot \text{kg}^{-1}$), at measured solubility points, are gathered in Table 7. The standard molar Gibbs free energy ($\Delta_{tr}G_{L-\text{arginine}}^o$) of transfer of L-arginine versus chloride salts molality, at different temperature is shown in Fig. 6.

From Fig. 6 and Table 7 clearly, the estimations of $\Delta_{tr}G_{AA}^o$ are positive. These outcomes demonstrated that the disintegration procedure of two studies on amino acid is a nonspontaneous process. Inside the temperature scope of the estimations, the $\Delta_{tr}G_{Glu}^o$ increases when chloride salts concentration is increasing, this happens when compounds are salting-out [37,38].

The general pattern obtained for the salting-out effect demonstrated a $\Delta_{tr}G_{Glu}^o$ decline in the following order: NaCl > KCl.

It is found that for both the amino acids, the ($\Delta_{tr}H^o$) values show a positive for aqueous NaCl solution and a negative in aqueous KCl solution, which indicated that the chemical stability of two amino acids is higher in NaCl–water system than in KCl–water system.

Table 7. The standard molar Gibbs energy $\Delta_{tr}G^o/(\text{J} \cdot \text{mol}^{-1})$, enthalpy $\Delta_{tr}H^o/(\text{kJ} \cdot \text{mol}^{-1})$ and entropy $\Delta_{tr}S^o/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$ of transfer from pure water to aqueous chloride solution ($1 \text{ mol} \cdot \text{kg}^{-1}$), at different temperature^a

Salt		298.15	303.15	308.15	313.15	318.15	323.15
L-arginine	NaCl	$\Delta_{tr}G^o$	250.031	436.803	584.432	745.307	804.934
		$\Delta_{tr}H^o$	10.498	10.535	10.570	10.604	10.670
		$\Delta_{tr}S^o$	34.372	33.310	32.405	31.483	29.808
	KCl	$\Delta_{tr}G^o$	122.343	317.419	441.654	547.191	574.277
		$\Delta_{tr}H^o$	-8.922	-8.114	-7.332	-6.575	-5.841
		$\Delta_{tr}S^o$	-30.335	-27.812	-25.226	-22.743	-20.165
L-histidine	NaCl	$\Delta_{tr}G^o$	569.223	530.980	466.809	429.603	378.856
		$\Delta_{tr}H^o$	4.749	3.942	3.161	2.405	1.673
		$\Delta_{tr}S^o$	14.019	11.252	8.744	6.309	4.068
	KCl	$\Delta_{tr}G^o$	410.204	319.571	288.763	238.444	266.623
		$\Delta_{tr}H^o$	-26.428	-27.349	-28.239	-29.102	-29.937
		$\Delta_{tr}S^o$	-90.016	-91.269	-92.579	-93.693	-94.934

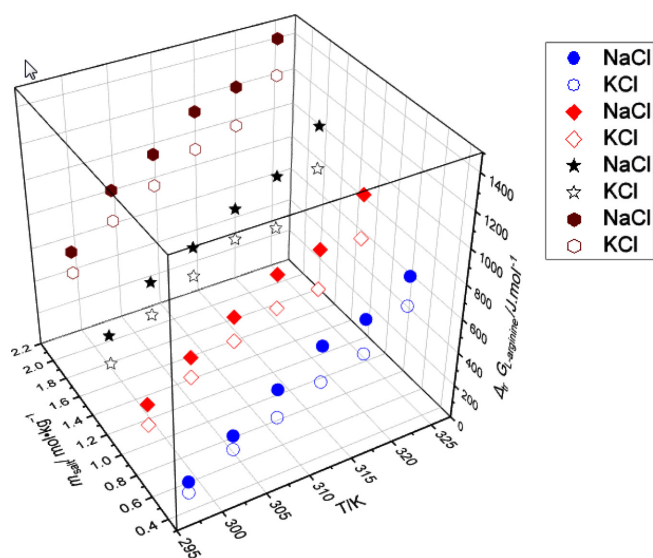


Fig. 6. Standard molar Gibbs free energy of transfer of L-arginine from water to aqueous chloride solutions, as functions of salt molality, at different temperatures.

The electrolytes sodium chloride and potassium chloride disrupt the hydrophobic hydration cosphere between the zwitterionic amino acids (i.e., L-arginine and L-histidine) and water molecules.

Fig. 6 affirms that the inclusion of KCl renders marginally simpler the solubility of L-arginine in water when compared to that of NaCl. Also, the rising of temperature prompts a simpler solubility of L-arginine in KCl solution (minimal $\Delta_{tr}G_{Glu}^{\circ}$ value). Similar outcomes were obtained from previous work [39] in studying the solubility of some phenolic compounds in water and in aqueous salts solutions at different temperatures. In every one of the cases the evaluated $\Delta_{tr}S_{Glu}^{\circ}$ values are negative, which proposes that an expansion in the system takes the exchange of AA from pure water to chloride aqueous solution to be unfavorable. $\Delta_{tr}S_{Glu}^{\circ}$ values are negative, which suggests that an increase in order in the system causes the transfer of AA from pure water to chloride aqueous solution to be unfavorable.

5. Conclusion

The main work was to measure and regress the solubility of L-arginine and L-histidine in aqueous chloride solutions under atmospheric pressure, with temperatures range from 298.15 to 323.15 K. The solubility increased with rising temperature, and decreased with the increase of the amount of chloride salts in the water, in all studied systems. The experimental solubility data of L-arginine and L-histidine in various aqueous chloride solutions were well correlated based on the semi-empirical equation. A salting-out effect of the electrolytic solutions under study (KCl and NaCl) was observed for L-arginine and L-histidine. The impact of the nature of the electrolytic salts under investigation concurred with that in the literature and happened in the following order: KCl > NaCl. Solubility and thermodynamics of parameters of transfer amino acids in aqueous solution may assume a

significant role in their biochemical and biophysical activities in human physiology.

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