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Interactions between several L-α-amino acids and potassium chloride in aqueous solutions at 298.15 K

Bartlomiej Palecz · Joanna Dunal

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Abstract The enthalpies of solution of L-α-aminobutyric acid, L-α-valine, L-α-leucine, L-α-isoleucine, and L-α-cysteine have been measured in aqueous potassium chloride solutions at 298.15 K. From the obtained experimental results the standard dissolution enthalpies of amino acids in aqueous KCl solutions have been determined. These data were used to calculate the heterogeneous enthalpic pair interaction coefficients based on McMillan–Mayer's theory. These values were interpreted in the terms of the hydrophobic or hydrophilic effects of the side chains of amino acids on their interactions with dissociated potassium chloride in water.

Keywords L-α-Amino acids aqueous solutions of KCl · Enthalpies of solution · Enthalpic pair interaction coefficients

List of symbols

h_{AE}	The heterogeneous enthalpic pair interaction coefficient between zwitterions of amino acids and dissociated potassium chloride
h_{AEE}	The enthalpic triplet interaction coefficient
$\Delta_{sol}H_{m}^{\infty}(W)$	Standard solution enthalpies of L-α-amino acids in water
$\Delta_{sol}H_{m}^{\infty}(W+E)$	Standard enthalpies of solution of the L-α-amino acids in aqueous solutions of potassium chloride (E)
m_E	Molal concentration of KCl in water (mol kg^{-1})

Introduction

Natural free L-α-amino acids existing in the tissues of living organisms participate not only in the processes of coding polypeptide chains but they also react with all the components dissolved in the tissue fluids. The basic ions occurring in the cytoplasm, responsible for the isotonic character of biological cells, playing an important role in the transport through biological membrane and participating in many metabolic processes, are potassium, sodium and chloride ions. Therefore, research into the interactions between zwitterions of amino acids and dissociated electrolytes in aqueous solutions can contribute to better learning and fuller understanding of the specificity of interactions, in which coded amino acids participate in the cytoplasmic space of a biological cell.

Our department, similarly as many other research centers, has carried out thermodynamic studied on the interactions between L-α-amino acids and electrolytes [1–3] or small organic molecules [4–7].

The aim of this study is to describe the interaction proceeding between the zwitterions of selected L-α-amino acids and dissociated potassium chloride in aqueous solutions.

The thermodynamic parameters that well describe the effects of energetic interactions between molecules in aqueous solutions include the enthalpic par interaction coefficients being derived from modified [8, 9] McMillan–Mayer's theory [10]. These coefficients describe the

B. Palecz (✉) · J. Dunal
Department of Physical Chemistry, University of Lodz,
90-416, Lodz, Poland
e-mail: paleczb@uni.lodz.pl

interactions between two homogeneous or heterogeneous molecules proceeding with the competitive co-contribution of solvent molecules, in our case water molecules.

In order to determine the enthalpic heterogenic pair interaction coefficients describing the energetic effects of interactions between selected zwitterions of amino acids and dissociated KCl, the enthalpies of solutions of the amino acids under discussion in aqueous solutions of potassium chloride were measured by the calorimetric method at a temperature of 298,15 K.

Experimental

Aminobutyric acid (Aba), valine (Val), leucine (Leu), isoleucine (Ile) and L-α-cysteine (Cys) (all mass fraction purity > 0.99, Fluka) were crystallized with aqueous ethanol solutions and dried under reduced pressure at 333 K for 72 h. KCl (mass fraction purity 0.995, Fluka) were dried under reduced pressure at $T = 373$ K. The water used in the experiments was deionized and distilled twice. The enthalpies of solution were measured in water and in aqueous solutions of potassium chloride using an isoperibol calorimeter [11]. The temperature sensitivity was about 4×10^{-5} K and the temperature stability of the thermostat was better than 2×10^{-3} K. The maximum error in the enthalpy measurements was ±0.5%. The examined aqueous solutions containing from 0 to 2.5 mol of KCl in 1 kg of water and the aqueous solutions of amino acids (A) (1×10^{-3} to 5×10^{-3}) mol (A) kg^{-1}(solvent) were prepared by weight using Mettler AE 240 balance within the precision $\pm 10^{-5}$ g (buoyancy corrections to the weights were ($\pm 2 \times 10^{-5}$ g). The standard enthalpies of solution of L-α-amino acids (A) were determined by the linear extrapolation to zero concentration of the results obtained for six to eight measurements within the investigated range of the amino acids concentration.

Results and discussion

The determined standard enthalpies of solution of the L-α-amino acids in aqueous solutions of potassium chloride (E) $\left\{\Delta_{\mathrm{sol}} H_{\mathrm{m}}^{\infty}(\mathrm{W}+\mathrm{E})\right\}$, together with their standard deviations, are presented in Table 1.

The values of standard dissolution enthalpies were used to obtain the enthalpic heterogeneous pair interaction coefficients by the equation proposed by Desnoyers [12]:

$$\begin{aligned}\Delta_{\mathrm{sol}} H_{\mathrm{m}}^{\infty}(\mathrm{W}+\mathrm{E}) &- \Delta_{\mathrm{sol}} H_{\mathrm{m}}^{\infty}(\mathrm{W}) \\ &= 2h_{\mathrm{AE}} m_{\mathrm{E}} + 3h_{\mathrm{AEE}} m_{\mathrm{E}}^{2} + \cdots \qquad (1)\end{aligned}$$

where $\Delta_{\mathrm{sol}}\mathrm{H}_{\mathrm{m}}^{\infty}(\mathrm{W})$ is the standard solution enthalpies of L-α-amino acids in water (see Table 1) h_{AE} is the heterogeneous enthalpic pair interaction coefficient between zwitterions of amino acids and dissociated potassium chloride (see Table 2), h_{AEE} is the enthalpic triplet interaction coefficient (see Table 2), and m_{E} denotes the molality concentration of KCl in water (mol kg^{-1}).

Table 2 The values of the heterogeneous pair and triplet interaction coefficients for L-α-amino acids with potassium chloride in water at $T = 298.15$ *K*

Amino acids	h_{AE}/(J kg mol^{-2})	h_{AE}/(J kg mol^{-2})	$\mathrm{CH_2}$
Gly[a]	−470.0		0.5
Ala[b]	−109.1 ± 5.5	14.8 ± 1.5	1.5
Aba	132.0 ± 9.0	−16.0 ± 4.0	2.5
Val	246.0 ± 8.0	−31.0 ± 2.0	3.5
Leu	278.0 ± 24.0	−32.0 ± 9.0	4.5
Ile	303.0 ± 37.0	−36.0 ± 10.0	4.5
Cys	−349.0 ± 24.0	42.0 ± 6.0	
Ser[b]	−612.0 ± 25.0	54.7 ± 6.5	
Thr[b]	−207.5 ± 8.0	24.8 ± 3.2	

[a] From Ref. [13]

[b] From Ref. [1]

Table 1 Standard enthalpies of solution of L-α-amino acids in aqueous potassium chloride solutions at $T = 298.15$ *K*

m_{E}/(mol kg^{-1})	$\Delta_{\mathrm{sol}} H_{\mathrm{m}}^{\infty}(\mathrm{W}+\mathrm{E})/\mathrm{kJ\,mol}^{-1}$				
	Aba	Val	Leu	Ile	Cys
0 00	0.795 ± 0.01[a]	3.12 ± 0.07[b]	3.41 ± 0.07[b]	3.06 ± 0.01[a]	11.15 ± 0.03[a]
0.25	0.830 ± 0.01	3.23 ± 0.02	3.55 ± 0.02	3.23 ± 0.02	10.92 ± 0.07
0.50	0.890 ± 0.01	3.34 ± 0.02	3.67 ± 0.02	3.42 ± 0.02	10.83 ± 0.06
0.75	0.960 ± 0.01	3.45 ± 0.02	3.76 ± 0.02	3.54 ± 0.02	10.61 ± 0.05
1.00	1.020 ± 0.01	3.51 ± 0.02	3.86 ± 0.03	3.66 ± 0.02	10.49 ± 0.05
1.50	1.070 ± 0.01	3.66 ± 0.03	4.05 ± 0.03	3.73 ± 0.03	10.17 ± 0.06
2.00	1.100 ± 0.01	3.73 ± 0.03	4.12 ± 0.03	3.85 ± 0.03	9.87 ± 0.06
2.50	1.150 ± 0.01	3.78 ± 0.03	4.20 ± 0.03	3.99 ± 0.03	9.55 ± 0.05

[a] From Ref. [15]

[b] From Ref. [20]

The values of h_{AE} are the sum of the effect of interaction between the L-α-amino acid zwitterion with the cation (M^+) and the anion (X^-) of KCl in aqueous solutions.

$$h_{AE} = h(A - M^+X^-) = h_{AM^+} + h_{AX^-} \qquad (2)$$

The interpretation of the triplet interaction coefficient is obscured by the fact that they also contain some contributions from the pairwise interaction terms, they are not discussed in this article.

The determined values of the enthalpic heterogenic pair interaction coefficients, h_{AE}, describe the energetic interactions between the hydrated zwitterions of the amino acid under investigation and the hydrated pair of cation and anion of potassium chloride in an aqueous solution. The described global effect of the interactions is a sum of several co-competitive processes:

(1) Exothermic interactions between the zwitterion "head" of amino acid $\left(-CHNH_3^+COO^-\right)$ and its polar side groups and dissociated electrolyte (as the sum of contributions of the cation and anion).
(2) Endothermic effects of partial dehydrations of hydration sheaths of ionic or polar groups of amino acids and ions (K^+, Cl^-).

Moreover, in the case of amino acids with non-polar side substituents, the phenomenon of hydrophobic hydration caused by these side substituents significantly influences the interactions discussed. The effect of intensified interactions between water molecules surrounding the non-polar amino acid groups is transferred onto the water molecules (co-operation of hydrogen bonds) that hydrate the zwitterions head of amino acid $\left(-CHNH_3^+COO^-\right)$ or polar side substituent. Consequently, the removal of some water molecules that constitute a hindrance to direct approach of reacting polar groups requires a higher energy input, which brings about increased endothermic effects. The determined values of the enthalpic pair interaction coefficients, h_{AE}, of the amino acids investigated and alkyl side substituents (Aba, Val, Leu, Ile) are positive (Table 2). They testify to dominating dehydration processes over the effects of direct interactions between the zwitterions of amino acids and dissociated potassium chloride in water. The values of the enthalpic heterogenic pair interaction coefficients h_{AE} (including glycine [13] and alanine [1]) increase with increasing number of carbon atoms in the side substituent.

The increase in the values of enthalpic heterogeneous interaction coefficients h_{AE} of the amino acids under consideration becomes smaller and smaller as the side chain is extended with additional CH_2 groups (Fig. 1) (according to Savage and Wood [14], it is accepted that the CH_3 group corresponds to 1.5 CH_2, while CH corresponds to 0.5 CH_2 see Table 2). The phenomena of hydrophobic hydration that reinforce the interactions between water molecules surrounding the more remote alkyl groups are transferred to a lesser extent onto water molecules that hydrate the zwitterion "head" of amino acid. Thus, the endothermic effect of partial dehydration of the solvation sheath in the polar portion of amino acid does not increase proportionally to the number of carbon atoms in the side chain, similarly as in aqueous solution of amino acids and NaCl [1] or amino acids and urea molecule [15].

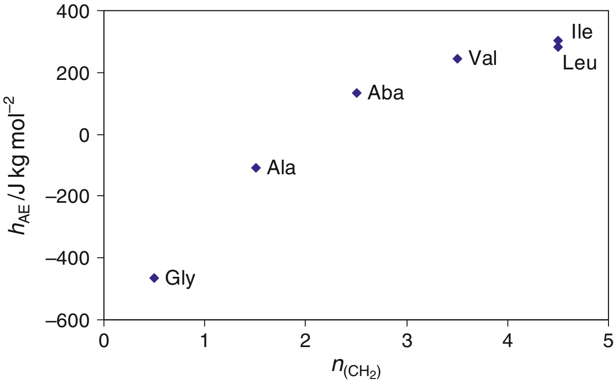

Fig. 1 The dependence of the enthalpic pair interaction coefficients of L-α-amino acids and KCl in water on the number of CH_2 groups in the side chain of amino acid molecule

The values of the enthalpic coefficient of interaction between the zwitterion of L-α-cysteine and dissociated potassium chloride are negative, which testifies to the dominating exothermic effects of direct interactions over the endothermic processes of partial dehydrations. The values of the enthalpic coefficient, $h_{(Cys-KCl)}$, of L-α-cysteine are more exothermic than those for L-α-alanine, but less exothermic that those for L-α-serine [1] (Table 2). The substitution of hydrogen atom in the alkyl side substituent of alanine with polar –SH group brings about a decrease in the value of the enthalpic coefficient of interaction between the zwitterion of cysteine and the dissociated electrolyte (see Table 2). This testifies to increase exothermic effects of direct interactions between the dissociated electrolyte and the amino acid with a polar side substituent that dominated over the processes of partial dehydration of ionic and polar groups. The replacement of hydrogen atom in the side substituent (–CH_3) of L-α-alanine with a strongly polar hydroxyl group, –OH (L-α-serine) brings about still higher drop in the enthalpic coefficient, h_{AE}, than in the case of L-α-cysteine.

Analyzing the values of enthalpic pair interaction coefficients of deionized potassium chloride and zwitterions of L-α-alanine, L-α-cysteine and L-α-serine, one can observe a decrease in the value of enthalpic coefficient h_{AE} with substitution of the alanine side chain with polar groups such

Table 3 Heterogeneous enthalpic pair interaction coefficients for amino acids with urea in water (h_{AU}) [17] and the free energy transfer of amino acids (ΔG_R) [18]

Amino acids	h_{AU}/(J kg mol^{-2}	ΔG_R/(kJ mol^{-1})
Gly	−390.2	0.00
Ala	−238.2	0.67
Val	−116.0	1.50
Leu	−98.0	1.90
Ile	−95.0	1.90
Ser	−511.0	0.01
Thr	−350.0	0.52
Cys	−358.0	0.38
Aba	−185.0	

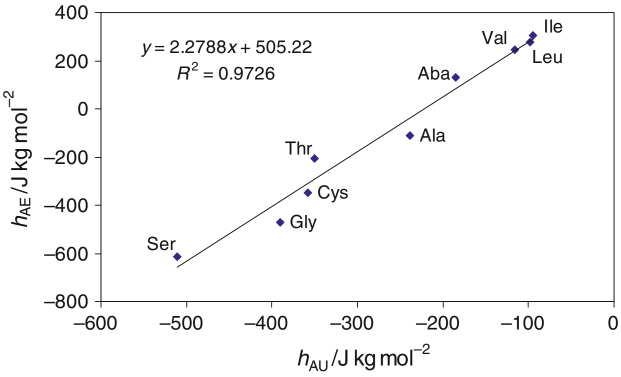

Fig. 2 Relationship between the enthalpic pair interaction coefficients h_{AU} of amino acids zwitterions–urea molecule in water [17] and the enthalpic pair interaction coefficients h_{AE} of amino acids zwitterions–potassium chloride in water

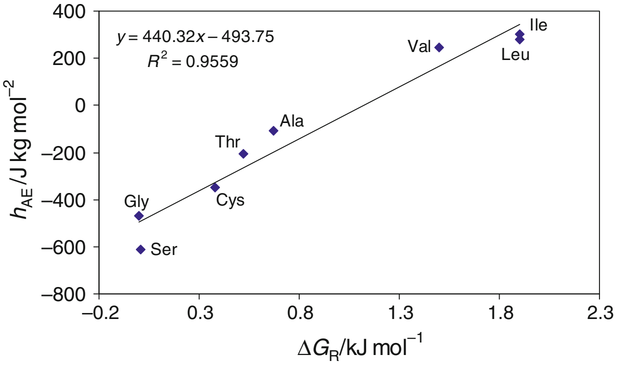

Fig. 3 Relationship between the hydrophobicity parameters of amino acids ΔG_R [18] and the enthalpic heterogenous pair interaction coefficients h_{AE} of the amino acids–potassium chloride in water

as –SH and –OH (Table 2). The values of enthalpic heterogeneous pair interaction coefficients of alanine and its derivatives change in the following sequence: $h_{(Ala-KCl)} > h_{(Cys-KCl)} > h_{(Ser-KCl)}$. The replacement of –SH with –OH brings about an increase in direct exothermic interactions between the deionized KCl and amino acids zwitterions, which seems to be caused by the greater ability of the –OH group of serine to form donor–acceptor bonds in comparison with the –SH group of cysteine [16].

The determined enthalpic coefficients (h_{AE}) of the interactions between the zwitterions of L-α-amino acid and dissociated potassium chloride in water (Table 2) are listed with the thermodynamic hydrophobicity scale of amino acid side substituents, determined on the basis of the enthalpic coefficients of the interactions between the zwitterions of L-α-amino acids and the molecule of urea in water h_{AU} [17] (Table 3). The presented linear relationship of coefficient $R^2 = 0.9726$ (Fig. 2) indicates similar contributions of the functional groups of amino acid side substituents to the global effects described by the enthalpic coefficients of interaction of heterogeneous pairs h_{AE} and h_{AU}.

By adding up the numerical values of the lipophilicity of amino acids or their side substituents appearing in the analyzed scales, an averaged scale of hydrophobicity of amino acids or their side chains was obtained. Analyzing the hydrophobicity scale by Eisenberg [18] (Table 3) shows a linear correlation ($R^2 = 0.9559$; see Fig. 3) between the averaged hydrophobicity parameters ΔG_R and heterogeneous enthalpic pair interaction coefficients for amino acids with potassium chloride in water h_{AE}. The developed scale well correlates with the obtained values of enthalpic interaction coefficients of heterogeneous pairs. These values according to Stryer [19] differentiate well the hydrophobicity of side amino acids chains, permitting to identify the helices of transmembranous proteins.

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