

The enthalpies of solution of α -alanine in water and in some alkali metal chloride solutions at 298.15 K

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Abstract

The enthalpies of solution of α -alanine were measured in water and in LiCl, NaCl and KCl solutions at 298.15 K, and the enthalpic interaction parameters h_{xy} , h_{xxy} and h_{xyy} of α -alanine with the three salts were evaluated. The dependences of the enthalpic interaction parameters on the ionic size of the electrolyte are discussed within the concepts of electrostatic and structural interactions.

Keywords: Alanine; Alkali metal chloride; Heat of solution; Water

1. Introduction

During the last decade, there has been considerable interest in the properties of ternary aqueous solutions containing amino acids, peptides and electrolytes. Many studies have been made on the enthalpic effects of interaction [1–5]. However, most of the studies refer to the enthalpic interaction parameters between one amino acid molecule and an electrolyte. The pair interaction parameters only reflect the interaction between electrolyte and non-electrolyte in very low concentrations. When the concentration is not very low, triplet and higher order interaction parameters are required to express the thermodynamic properties of multi-component solutions.

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According to the McMillan–Mayer approach [6], all the thermodynamic properties of a multi-component solution can be expressed as a series of pair, triplet and higher order interaction terms between like and unlike solutes. The transfer enthalpy of a non-electrolyte (y) from pure water to an electrolyte (x) solution is [7,8]

$$\Delta H_y(w \rightarrow w + x) = 2vh_{xy}m_x + 3v^2h_{xxy}m_x^2 + 3vh_{xxy}m_xm_y + \dots \quad (1)$$

where m_x and m_y are the molalities defined per kg of pure water, v is the number of ions dissociated by the electrolyte (x), and the h_{xy} , h_{xxy} and h_{xyy} terms are enthalpic parameters representing interaction between the subscripted species.

The purpose of the present paper is to determine the molar transfer enthalpies of α -alanine from water to LiCl, NaCl and KCl solutions, using Eq. (1) to obtain the enthalpic interaction parameters.

2. Experimental

The enthalpies of solution were determined using a C-80 calorimeter (Setaram). The experimental procedure and purification of the materials have been described in earlier publications [9,10]. The total uncertainty in the enthalpy of solution was about $\pm 0.5\%$.

3. Results and discussion

The molar enthalpies of solution of α -alanine in water and in LiCl, NaCl and KCl solutions are given in Table 1.

There is a very good linear relation between the molar enthalpies of solution of α -alanine in water and its molalities in the range of concentration measured. The relation was obtained with the method of least-squares as follows:

$$\Delta_{sd}H_m/(\text{J mol}^{-1}) = 9253 + 271m_y \quad (2)$$

The standard derivation of the equation is $\pm 5 \text{ J mol}^{-1}$. The molar enthalpy of solution at infinite dilution of α -alanine, 9253 J mol^{-1} , is in good agreement with the literature values of 9250 J mol^{-1} [11], 9247 J mol^{-1} [12]. The enthalpies of transfer $\Delta H_y(w \rightarrow w + x)$ are the differences between the measured enthalpies of solution in electrolyte solutions and the enthalpies of solution in water which were calculated using Eq. (2).

Cassel and Wood [13] have compared some data and pointed out that in a variety of solutes having a concentration of 1 M, the pair term makes a contribution of from $+300$ to $-300 \text{ cal mol}^{-1}$ to the excess enthalpy of a solution, the triplet terms contribute $\pm 30 \text{ cal mol}^{-1}$, and the quadruplet $\pm 5 \text{ cal mol}^{-1}$. Therefore, within the experimental uncertainty the contribution of quadruplet and higher order terms to the enthalpy of transfer is negligible. Hence

$$\Delta H_y(w \rightarrow w + x)/m_x = 2vh_{xy} + 3v^2h_{xxy}m_x + 3vh_{xxy}m_y + \dots \quad (3)$$

Table 1
The enthalpies of solution ΔH_m of α -alanine in water–KCl mixtures at 298.15 K (in J mol⁻¹)

m_y in mol kg ⁻¹	ΔH_m water	m_y in mol kg ⁻¹	ΔH_m $m_x = 0.9995$	m_y in mol kg ⁻¹	ΔH_m $m_x = 2.9984$	m_y in mol kg ⁻¹	ΔH_m $m_x = 3.9930$
0.1364	9284	0.1449	9039	0.1554	9035	0.1583	9158
0.2099	9317	0.2170	9063	0.2354	9062	0.2356	9185
0.2794	9330	0.2878	9089	0.3038	9130	0.3094	9210
0.3427	9351	0.3573	9128	0.3842	9152	0.3806	9219
0.4119	9359	0.4258	9146	0.4583	9181	0.4556	9250
0.4838	9385	0.5036	9176	0.5386	9209	0.5308	9297

m_y in mol kg ⁻¹	ΔH_m water	m_y in mol kg ⁻¹	ΔH_m $m_x = 0.9980$	m_y in mol kg ⁻¹	ΔH_m $m_x = 3.0001$	m_y in mol kg ⁻¹	ΔH_m $m_x = 4.9794$
0.1427	9288	0.1402	9140	0.1789	9258	0.2064	10050
0.2100	9315	0.2151	9152	0.2515	9297	0.2839	10090
0.2833	9329	0.2822	9175	0.3205	9322	0.3653	10120
0.3458	9352	0.3501	9192	0.3963	9374	0.4385	10160
0.4236	9364	0.4263	9214	0.4623	9409	0.5060	10200
0.4884	9383	0.4901	9227	0.5313	9432	0.5880	10220

m_y in mol kg ⁻¹	ΔH_m water	m_y in mol kg ⁻¹	ΔH_m $m_x = 0.9996$	m_y in mol kg ⁻¹	ΔH_m $m_x = 2.9930$	m_y in mol kg ⁻¹	ΔH_m $m_x = 4.9954$
0.1451	9395	0.1433	9734	0.1530	10330	0.1474	10530
0.2187	9317	0.2130	9762	0.2167	10350	0.2219	10560
0.2900	9334	0.2831	9806	0.2811	10370	0.2952	10580
0.3528	9357	0.3520	9810	0.3545	10380	0.3720	10590
0.4283	9369	0.4236	9824	0.4335	10390	0.4437	10600
0.4923	9391	0.4875	9837	0.5016	10420	0.5164	10620

The enthalpies of solution ΔH_m of α -alanine in water–NaCl mixtures at 298.15 K (in J mol⁻¹)

The enthalpies of solution ΔH_m of α -alanine in water–LiCl mixtures at 298.15 K (in J mol⁻¹)

Table 2

The enthalpic interaction parameters of α -alanine with some electrolytes in water at 298.15 K

Electrolyte	h_{xy} in J kg mol ⁻²	h_{xyy} in J kg ² mol ⁻³	h_{xxy} in J kg ² mol ⁻³
LiCl	253 ± 3	-25 ± 5	-17 ± 1
NaCl	-123 ± 2	12 ± 3	23 ± 1
KCl	-160 ± 5	23 ± 8	26 ± 1

The enthalpies of transfer have been fitted to Eq. (3) using a least-squares routine and the enthalpic interaction parameters obtained are given in Table 2.

Equation (3) indicates that when m_x is fixed, $H_y(w \rightarrow w+x)/m_x$ is a linear function of m_y and the slope is not dependent on m_x . The interval between two lines with different m_x values is dependent on the h_{xxy} value and the difference in the two m_x values. The experimental relations of $H_y(w \rightarrow w+x)/m_x$ with m_x and m_y are shown in Figs. 1–3.

It is apparent from Table 2 that h_{xy} decreases from positive to negative values, whereas h_{xyy} and h_{xxy} increase from negative to positive values, as the size of the cation increases. This indicates different contributions from the interactions of electrolyte and non-electrolyte to the values of h_{xy} , h_{xxy} and h_{xyy} .

For the enthalpic effect, the interactions between electrolyte and zwitterionic ion, like α -alanine, mainly consist of two principal contributions, i.e. the electrostatic and structural terms. The structural interactions include the partial desolvation of solutes when they interact with each other and the solvent reorganisation arising from changes in the solvent adjacent to the solute molecules as they approach each other. Visser et al. [14] have published a general discussion of structural interactions

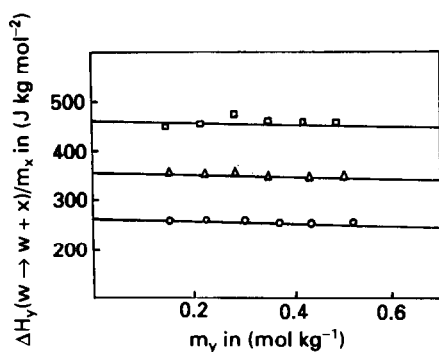


Fig. 1. Dependences of the function $\Delta H_y(w \rightarrow w+x)/m_x$ on m_x and m_y for the LiCl–water– α -alanine system at 298.15 K: \square , $m_x = 0.9996$; \triangle , $m_x = 2.9930$; \circ , $m_x = 4.9954$.

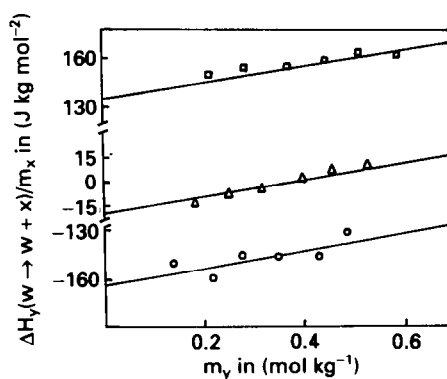


Fig. 2. Dependences of the function $\Delta H_y(w \rightarrow w+x)/m_x$ on m_x and m_y for the NaCl–water– α -alanine system at 298.15 K: \square , $m_x = 4.9794$; \triangle , $m_x = 3.0001$; \circ , $m_x = 0.9980$.

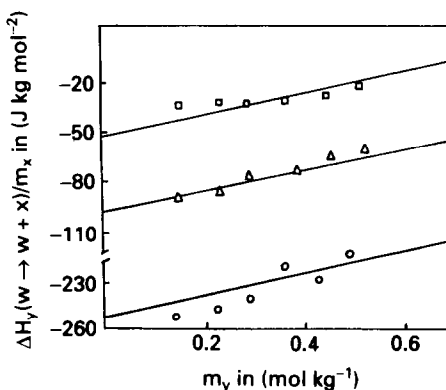


Fig. 3. Dependences of the function $\Delta H_y(w \rightarrow w + x)/m_x$ on m_x and m_y for the KCl–water– α -alanine system at 298.15 K: \square , $m_x = 3.9930$; Δ , $m_x = 2.9984$; \circ , $m_x = 0.9995$.

and believe that in most cases the net effect of cosphere overlap in the hydration structure is destructive. Structural interaction makes quite a large contribution to the enthalpic function and sometimes even becomes predominant [8,15].

In the present paper, it is assumed that the experimental enthalpic interaction parameters for the systems are ion additive and the chloride ion plays an invariant role in each system. Therefore, the properties of the cations are responsible for the observed trend.

Using Kirkwood's electrostatic theory [16,17], we may estimate the electrostatic contributions to the h_{xy} values from the equation

$$h_{xy}^{\text{elec}} = -RT^2 \left\{ (2A_1/(DT)^2 - A_2/(DT)) \left[(\partial \ln D/\partial T)_p + T^{-1} \right] + [(\partial d/\partial T)_p d^{-1} A_2/(DT)] \right\} \quad (4)$$

where d and D are the density and dielectric constant of the pure solvent and the terms A_1 and A_2 are given by $A_1 = 3.42 \times 10^6 \mu^2/a$ and $A_2 = 1.25 \times 10^2 V_A \alpha(\rho)/a$, where μ is the dipole moment of the dipolar ion, V_A the molar volume of the non-electrolyte, a the sum of the radii of the ionic component and the dipolar ion, and $\alpha(\rho)$, in which $\rho = b/a$, b being the radius of the non-electrolyte, is a function which has been tabulated. In calculating the electrostatic contributions to the enthalpic pairwise parameters, the following values were used $\mu = 13.7D$ [2], $V_A = 73.3 \text{ cm}^3 \text{ mol}^{-1}$ [2], $D = 78.54$ [18], $(\partial \ln D/\partial T)_p = -4.55 \times 10^{-3} \text{ K}^{-1}$ [18], and $(\partial d/\partial T)_p = -2.56 \times 10^{-4} \text{ g cm}^{-3} \text{ K}^{-1}$ [19], as well as the radii of the ionic components and dipolar ions [20,21]. The results are given in Table 3, together with the values of α -alanine with other alkali metal chlorides systems.

It is apparent that the values from electrostatic predictions are all positive and approximately the same, which is not in accordance with the experimental results. A general explanation is that Kirkwood's theory mainly refers to the electrostatic interactions. However, in addition to the electrostatic combinations, interactions between amino acids and salts are mainly structural interactions, such as the

Table 3

The comparison between experimental and calculated h_{xy} values in J kg mol^{-2}

Electrolyte	h_{xy}^{expt}	h_{xy}^{elec}	$\Delta h_{xy} = h_{xy}^{\text{expt}} - h_{xy}^{\text{elec}}$
LiCl	253	395	-142
NaCl	-123	383	-506
KCl	-160	370	-530
KBr ^a	-303	365	-668
KI ^a	-531	360	-891

^a From ref. [10].

breaking and making of water structure, the overlap of the cosphere of hydration, and particular hydrophobic interactions, ect. It is these structural factors that lead to the trends in h_{xy} values.

The interaction of electrolyte with an α -alanine molecule probably occurs at the zwitterionic head group of the α -alanine molecule. The contributions of the structural effects depend strongly on the solute type. The hydration cosphere of the lithium ion is thought to contain more hydration bonds than bulk water; the cosphere overlap of hydrophilic hydration of the polar part of α -alanine with that of lithium ion leads to a net destruction of some of the lithium cosphere, a relaxation of structured water to bulk water, and a positive contribution of the h_{xy} value. Because the hydration cosphere of the sodium and potassium ions are not like that of the lithium ion, the overlap of the structure-breaking regions of water in the cospheres close to the ions and the polar of the α -alanine molecule will make a large negative contribution to the h_{xy} values. In addition, the desolvation of the ions will become increasingly easier as the ionic size increases, and it would be expected that the net desolvation contribution will decrease as the ionic size increases. The structural effects mentioned above are the main reasons for the negative values of h_{xy} decreasing as the ionic size decreases.

Apart from the hydrophilic hydration of the polar part of α -alanine, there is also a hydrophobic hydration cosphere for the alkyl side-chain and the electrolyte ions will perturb the cosphere of the hydrocarbon part of α -alanine. The order of effectiveness of the electrolyte ions in reducing hydrophobic hydration is $\text{Li}^+ < \text{Na}^+ < \text{K}^+$; therefore, the positive contribution will be greater as the ionic size increases. The structural interactions of the electrolyte with the polar and non-polar groups of α -alanine have opposite effects on the ionic size dependence of h_{xy} . The observed trend suggests that the former structural interaction is predominant.

The h_{xxy} parameter is the mean ionic interaction of two electrolytes with an α -alanine molecule. It is clear that after an electrolyte has interacted with the polar groups of an α -alanine molecule, the other electrolyte will mainly interact with the non-polar groups of α -alanine, resulting in a destructive effect which will cause h_{xxy} to tend to be positive. The larger the ionic size of an electrolyte, the greater the destructive effect. The negative value of the h_{xxy} of α -alanine with LiCl suggests that

the structural interaction has little effect on the h_{xyy} values compared with the electrostatic interaction.

The h_{xyy} is the enthalpic interaction parameter of two α -alanine molecules with an electrolyte. In the case of the self-interaction between α -alanine molecules, the interactions are predominantly of a dipole–dipole nature, and head group effects prevail in side-chain interaction. An analysis for the h_{xyy} parameters presented in Table 2 indicates that the principal interaction between an electrolyte and a pair of α -alanine molecules is structural. Because a larger ion causes a larger disturbance to the hydration structure of the α -alanine, the h_{xyy} parameters increase from negative to positive as the ionic size increases.

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