View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by Biblioteca Digital do IPB

ChemPor 2014

U.PORTO

FEUP FACULDADE DE ENGENHARIA UNIVERSIDADE DO PORTO

ORDEM DOS ENGENHEIROS

10 – 12 Sept. 2014

PORTO

PORTUGAL

12th International Chemical and Biological Engineering Conference

BOOK OF EXTENDED ABSTRACTS

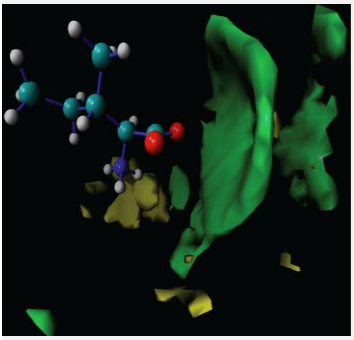
FEUP EDIÇÕES

9 789727 521708

Partial Molar Volumes of Glycine and L-Alanine in Aqueous $MgSO_4$ Solutions between 278.15 and 308.15 K

P-BE45

C.C. Mota[1], O. Ferreira[1], S. Pinho[1,2]. (1) Associate Laboratory LSRE/LCM, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5301-857 Bragança, Portugal, (2) UNIFACS-Universidade de Salvador, Rua Dr. José Peroba 251, CEP 41770-235 Salvador, Brasil; *spinho@ipb.pt.*



In this work, partial molar volumes of glycine and L-alanine in aqueous solutions of magnesium sulphate at (0.0, 0.1, 0.3, 0.7 and 1.0) molal were obtained between 278.15 K and 308.15 K. Additionally, partial molar volumes of transfer at infinite dilution and hydration numbers were calculated. In general, transfer volumes are higher for glycine then L-alanine. From the transfer volumes, it can be concluded that the predominant interactions are pairwise between ions and zwitterionic centers of the amino acids. On the other hand, hydration numbers are higher for L-alanine than glycine. Dehydration of the studied amino acids is observed, rising either temperature or salt molality.

Background

Amino acids are the building blocks and model compounds of proteins, besides having a wide variety of applications in the food, pharmaceutical and chemical areas. In biological systems, the frequent presence of ions plays an important role in the conformational stability of proteins. Therefore, the characterization of the type of interactions present in these systems is essential for the design of processes of extraction, purification or crystallization, as well as in the interpretation of fundamental biochemical mechanisms.

Salts have effect on the properties and structural stability of proteins that includes their solubility, denaturation, dissociation into subunits and activity of enzymes [1]. A high salt concentration of Na_2SO_4, CH_3COONa and $MgSO_4$ stabilizes proteins whereas salts such as $MgCl_2$, $CaCl_2$ and KSCN denature proteins [2].

In view of the importance of $MgSO_4$ in altering the conformational stability of proteins, it is important to understand the interaction of their building blocks with that salt, to search for the mechanisms beyond the stabilization phenomena [3].

Objectives

The aim of this work is to calculate the partial molar volumes (PMV) of glycine (Gly) and L-alanine (Ala) in aqueous solutions of magnesium sulphate at (0.0, 0.1, 0.3, 0.7 and 1.0) molal, in the temperature range from 278.15 K to 308.15 K. The density data will also be used to calculate partial molar volumes of transfer and hydration numbers.

All these data are explored in order to interpret the interactions in solution, their magnitude and comparisons among other amino acids or salts.

Methods

The density measurements were performed using a vibrating-tube densimeter with a U-shaped glass tube (DMA 5000 M, Anton Paar, Graz, Austria). For each set of measurements, the densimeter was calibrated at 20 ºC with dry air and water, and at each temperature a water check was performed and compared to literature values [4], which must be within a few units of the order 10^{-3} kg·m^{-3}. The measurement repeatability of density is ±1x10^{-2} kg·m^{-3} and 1 mK for temperature.

Results

From the density data, the partial molar volume ($V^o_{m,A}$) of the amino acid at infinite dilution is calculated by:

$$V^o_{m,A} = \frac{M_A}{\rho_0} - \frac{1 + m_s M_s}{\rho_0^2} a_v \qquad (1)$$

Where M_A and M_s are the molar mass of the amino acid and salt, respectively, m_s is the molality of the salt, and ρ_0 is the density of solvent (pure water or binary water + salt solvent). The parameter a_v is obtained by representing the experimental density data in the linear form:

$$\frac{\rho - \rho_0}{m_A} = a_v + b_v m_A \qquad (2)$$

In equation (2) ρ is the density of the solution, m_A is the amino acid molality, and b_v is the slope of the linear equation.

Following the approach presented here, at all salt molalities and temperatures, a very good linear fit was found using Equation (2).

The partial molar volumes of the amino acids studied in this work are presented in Figure 1.

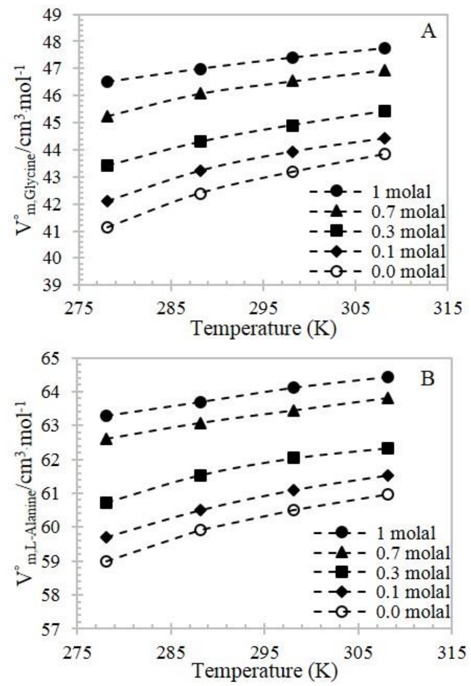


Figure 1. Partial molar volumes at infinite dilution of the amino acid, at different temperatures and salt molalities (lines are to aid the eye): A. Gly and B. Ala.

As shown in Figure 1, the PMV of the amino acid increases with salt molality and temperature, which is in line with the interpretation that both factors reduce the electrostriction of water around the amino acid. In particular, in the vicinity of the charged groups COO^- and NH_3^+, those water molecules are more like bulk water, giving an increase in the volume of the amino acids.

To check the quality of the data, the calculated partial molar volumes in water were compared to Talele and Kishore [5], Martins *et al.* [6] and the average values calculated by Zhao [7] at 298.15 K. This comparison is presented in Table 1.

Table 1. Comparison of PMV obtained in this work with literature.

Amino acid	This work	[5]	[6]	[7]
Gly	43.17	43.14	43.20	43.18
Ala	60.51	60.43	60.46	60.48

By analysing Table 1, it can be concluded that the results of this work are in good agreement with literature.

Another consistency test that can be applied to the data is a comparison between the values of the partial molar expansion, $E^{o}_{m,A} = \left(\partial V^{o}_{m,A}/\partial T\right)_p$. For that, the partial molar volumes at infinite dilution in water were fitted to:

$$V^{o}_{m,A} = a + bT + cT^2 \qquad (3)$$

Where T is the absolute temperature, and a, b and c empirical constants. Figure 2 presents a comparison between the partial molar expansions (PME) of the amino acids studied in this work and PME values found in literature [6-10].

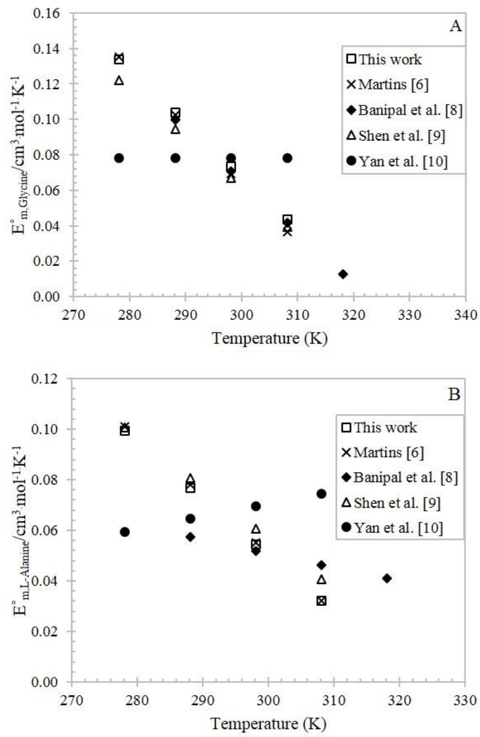


Figure 2. Comparison of PME of Gly (A) and Ala (B) in aqueous solutions.

As can be seen in Figure 2, the PME values obtained in this study are consistent with the authors mentioned above, except for the results reported by Yan *et al.* [10].

Partial Molar Volumes of Transfer

The partial molar volumes of transfer at infinite dilution $\Delta_{tr}\bar{V}_{m,A}$ from water to aqueous magnesium sulphate solutions have been calculated using Equation (4) and are listed in Table 2.

$$\Delta_{tr}\bar{V}_{m,A} = \bar{V}_{m,A}(\text{in aqueous salt solution}) -$$

$$-V_{m,A}(\text{in water}) \quad (4)$$

Table 2. Partial molar volumes of transfer at infinite dilution for Gly and Ala at different temperatures and magnesium sulphate molalities.

m_s/mol·kg^{-1}	$\Delta_{tr}V^{o}_{m,A}$/cm^3·mol^{-1}			
	278.15K	288.15K	298.15K	308.15K
	Glycine			
0.1	0.96	0.83	0.76	0.60
0.3	2.29	1.90	1.73	1.58
0.7	4.12	3.69	3.36	3.12
1.0	5.38	4.60	4.23	3.92
	L-alanine			
0.1	0.72	0.59	0.58	0.54
0.3	1.73	1.63	1.53	1.36
0.7	3.61	3.16	2.93	2.83
1.0	4.28	3.77	3.60	3.45

Partial molar volumes of transfer at infinite dilution increase with increasing salt molality or decreasing temperature.

According the co-sphere overlap model [11], some considerations can be made:

- The positive transfer volumes obtained here indicate the predominance of interactions between ions (Mg^{2+}, SO_4^{2-}) and zwitterionic centers of the amino acids ($-COO^-$, $-NH_3^+$);

- The presence of an additional hydrophobic -CH_2- group in alanine, compared to glycine, causes a reduction of $\Delta_{tr}V^{o}_{m,A}$.

Hydration numbers

Table 3 reports the hydration numbers calculated for both amino acids. As can be seen, they are larger for Ala, at the same experimental, conditions.

Also, amino acids dehydration increases both with salt molality and temperature. For glycine, when salt molality increases, the decrease in the hydration number is larger than for L-alanine but, when temperature increases, the opposite effect is observed.

Table 3. Hydration numbers of Gly and Ala at different temperatures and salt molalities.

m_s/mol·kg^{-1}	n_H			
	278.15K	288.15K	298.15K	308.15K
	Glycine			
0.0	4.13	3.27	2.64	2.01
0.1	3.76	2.98	2.40	1.86
0.3	3.25	2.61	2.11	1.61
0.7	2.55	2.00	1.62	1.23
1.0	2.06	1.68	1.35	1.03
	L-alanine			
0.0	4.91	4.08	3.41	2.69
0.1	4.63	3.88	3.23	2.56
0.3	4.24	3.52	2.94	2.35
0.7	3.52	2.99	2.52	1.98
1.0	3.26	2.78	2.31	1.83

Conclusions

Partial molar volumes at infinite dilution of Gly and Ala were obtained from density measurements, between 278.15 K and 308.15 K.

These data were used to calculate the partial molar volumes of transfer and hydration numbers.

Extending this study to other amino acids, peptides and salts, important physico-chemical parameters of those solutions are obtained and interpreted, relating the structure of amino acids and ion characteristics such as radius, charge and polarizability.

Acknowledgements

This work is supported by project Project PEst-C/EQB/LA0020/2013, financed by FEDER through COMPETE - Programa Operacional Factores de Competitividade and by FCT - Fundação para a Ciência e a Tecnologia. This work was also co-financed by QREN, ON2 and FEDER (Project NORTE-07-0162-FEDER-000050).

References

[1] J. J. Wang, Z. N. Yan, K. L. Zhuo, J. S. Lu, *Biophysical Chemistry*, 80 (1999) 179.
[2] T. Arakawa, S. N. Timasheff, *Biochemistry*, 23 (1984) 5912.
[3] B. C. Mallick, N. Kishore, *Journal of Solution Chemistry*, 35 (2006) 1441.
[4] F. Spieweck, H. Bettin, *Technisches Messen*, 59 (1992) 285.
[5] P. Talele, N. Kishore, *The Journal of Chemical Thermodynamics*, 70 (2014) 182.
[6] M. A. R. Martins, Densities and Speed of Sound in Aqueous Ammonium Sulfate Solutions Containing Glycine or Alanine, Master Thesis, Instituto Politécnico de Bragança, 2013.
[7] H. Zhao, Biophysical Chemistry, 122 (2006) 157.
[8] T. S. Banipal, J. Kaur, P. K. Banipal, K. Singh, *The Journal of Chemical and Engineering Data*, 53 (2008) 1803.
[9] J. L. Shen, Z. F. Li, B. H. Wang, Y. M. Zhang, *The Journal of Chemical Thermodynamics*, 32 (2000) 805.
[10] Z. N. Yan, J. J. Wang, W. B. Liu, J. S. Lu, *Thermochimica Acta*, 334 (1999) 17.
[11] H.S. Frank, M.W. Evans, *The Journal of Chemical Physics*,13 (1945) 507.