Thermochimica Acta 478 (2008) 54–56

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Short communication

A calorimetric study on interactions of amino acids with sodium dodecylsulfate and dodecyltrimethylammonium bromide in aqueous solutions at 298.15 K

Xiaomei Qiu, Qunfang Lei, Wenjun Fang*, Ruisen Lin

Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China

ARTICLE INFO

Article history:
Received 8 March 2008
Received in revised form 31 August 2008
Accepted 4 September 2008
Available online 11 September 2008

Keywords:
Amino acid
Enthalpy of transfer
Surfactant solution

ABSTRACT

Enthalpies of solution and transfer of glycine, L-alanine, L-valine, L-serine and L-threonine from water to aqueous surfactant (sodium dodecyl sulfate or dodecyltrimethylammonium bromide) solutions have been determined at 298.15 K by isothermal calorimetry. Dehydration and ion–ion interactions are important at low concentrations of the surfactant. Hydrophobic–hydrophobic interactions become primary when the amino acid molecules insert into the hydrophobic tail groups of the micelles. These phenomena can be explained with the hydration co-sphere overlap model.

1. Introduction

Amino acids are useful probe molecules for determining functional group contributions to biopolymer conformational stability [1–12]. Interactions between surfactant and protein molecules are a subject of intensive research because they can modulate the functional properties of protein molecules. However, details of the interactions remain unclear [13–20]. The present work reports the enthalpies of transfer of glycine, L-alanine, L-valine, L-serine and L-threonine from water to aqueous sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium bromide (DTAB) solutions at 298.15 K to obtain information about hydrophobic and hydrophilic interactions of amino acids of different molecular structure.

2. Experimental

2.1. Reagents

Five amino acids ($RCH(NH_2)COOH$), glycine ($R=H$), L-alanine ($R=CH_3$), L-valine ($R=CH(CH_3)_2$), L-serine ($R=CH_2OH$) and L-threonine ($R=CH_2(OH)CH_3$) (biological reagent, mass fraction >99%, Shanghai Chemical Co., China), were twice recrystallized from aqueous ethanol solution and dried under vacuum at 348 K for 6 h before use. Two surfactants, sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium bromide (DTAB), were products of Sigma (purity >99%). All the solutions were freshly prepared with twice-distilled water. The final molality of each amino acid was $0.1000 \pm 0.0002\ \mathrm{mol\,kg^{-1}}$. The concentrations of the surfactants are above their critical micelle concentrations (CMC), which are 8.1×10^{-3} and $15.9 \times 10^{-3}\ \mathrm{mol\,dm^{-3}}$, respectively [21,22].

2.2. Calorimetric procedure

Measurements on the enthalpies of solution were carried out with an RD496-II calorimeter (manufactured by the 2905 Factory of the Nuclear Industry Department of China) at 298.15 K as described in detail previously [10]. The calorimeter was calibrated by the solution enthalpy of KCl in water with the mole ratio of 1:500. The calorimetric measurements for each sample were performed at least twice and average values are reported.

3. Results and discussion

The enthalpies of solution, $\Delta_{\mathrm{sol}}H_{\mathrm{m}}$, in pure water and in different concentrations of surfactant are presented in Table 1. The values of $\Delta_{\mathrm{sol}}H_{\mathrm{m}}$ for the amino acids in water agree well with reference data [11,12]. All of the $\Delta_{\mathrm{sol}}H_{\mathrm{m}}$ values are positive, *i.e.*, endothermic.

The enthalpies of transfer, $\Delta_{\mathrm{tr}}H_{\mathrm{m}}$, were derived from the differences between the enthalpies of solution of amino acids in surfactant solutions, $\Delta_{\mathrm{sol}}H_{\mathrm{m(s)}}$, and those in pure water, $\Delta_{\mathrm{sol}}H_{\mathrm{m(w)}}$ [8]:

$$\Delta_{\mathrm{tr}}H_{\mathrm{m}} = \Delta_{\mathrm{sol}}H_{\mathrm{m(s)}} - \Delta_{\mathrm{sol}}H_{\mathrm{m(w)}} \qquad (1)$$

Figs. 1 and 2 show the changes of $\Delta_{\mathrm{tr}}H_{\mathrm{m}}$ with the different molalities of surfactant. In the ternary solutions (amino acid + SDS/DTAB + water), the trend of $\Delta_{\mathrm{tr}}H_{\mathrm{m}}$ can be divided into three parts.

---

* Corresponding author. Tel.: +86 571 87952371; fax: +86 571 87951895.
E-mail address: fwjun@zju.edu.cn (W. Fang).

0040-6031/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2008.09.001

Table 1
Enthalpies of solution $\Delta_{sol}H_m$ of amino acids in aqueous surfactant solutions at 298.15 K

Surfactant	m_{sur} ($\times 10^3$ mol kg^{-1})	$\Delta_{sol}H_m$ (kJ mol^{-1})				
		Glycine	L-Alanine	L-Valine	L-Serine	L-Threonine
	0	14.17[a] ± 0.02	7.60[a] ± 0.01	3.15[a] ± 0.01	11.30[a] ± 0.03	10.35[a] ± 0.01
	0	14.20[b]	7.67[b]	3.12[b]	11.49[c]	10.33[c]
SDS	9.88	14.17 ± 0.01	7.63 ± 0.01	3.22 ± 0.01	11.29 ± 0.02	10.42 ± 0.01
	19.64	14.31 ± 0.04	7.80 ± 0.02	3.38 ± 0.03	11.43 ± 0.01	10.63 ± 0.04
	29.86	14.47 ± 0.01	7.94 ± 0.04	3.55 ± 0.03	11.65 ± 0.04	10.81 ± 0.01
	39.73	14.55 ± 0.01	8.08 ± 0.02	3.65 ± 0.02	11.70 ± 0.01	10.92 ± 0.01
	49.64	14.67 ± 0.05	8.15 ± 0.01	3.74 ± 0.01	11.79 ± 0.02	10.97 ± 0.03
	59.74	14.00 ± 0.01	7.57 ± 0.03	3.55 ± 0.02	11.19 ± 0.01	10.86 ± 0.01
	69.65	13.86 ± 0.02	7.42 ± 0.02	3.16 ± 0.01	11.11 ± 0.03	10.54 ± 0.02
	79.89	13.94 ± 0.02	7.57 ± 0.01	3.56 ± 0.01	11.34 ± 0.01	10.92 ± 0.03
	89.96	14.17 ± 0.02	7.78 ± 0.01	3.65 ± 0.05	11.57 ± 0.01	11.08 ± 0.02
	99.72	14.28 ± 0.03	7.86 ± 0.02	3.76 ± 0.02	11.68 ± 0.01	11.18 ± 0.01
DTAB	10.14	14.14 ± 0.01	7.63 ± 0.03	3.18 ± 0.02	11.29 ± 0.01	10.38 ± 0.01
	19.66	14.38 ± 0.04	7.86 ± 0.01	3.48 ± 0.01	11.58 ± 0.03	10.71 ± 0.04
	30.75	14.68 ± 0.01	8.18 ± 0.01	3.75 ± 0.02	11.83 ± 0.02	10.98 ± 0.01
	39.91	14.27 ± 0.03	7.91 ± 0.01	3.60 ± 0.01	11.54 ± 0.01	10.95 ± 0.02
	49.69	14.09 ± 0.02	7.75 ± 0.05	3.41 ± 0.03	11.42 ± 0.04	10.86 ± 0.03
	59.81	13.80 ± 0.03	7.41 ± 0.02	3.31 ± 0.02	11.24 ± 0.01	10.67 ± 0.01
	69.78	13.91 ± 0.03	7.61 ± 0.02	3.51 ± 0.01	11.38 ± 0.03	10.87 ± 0.01
	79.65	14.05 ± 0.01	7.78 ± 0.03	3.67 ± 0.03	11.41 ± 0.01	11.01 ± 0.02
	89.88	14.17 ± 0.01	7.85 ± 0.01	3.76 ± 0.02	11.50 ± 0.03	11.11 ± 0.03
	100.0	14.30 ± 0.01	7.93 ± 0.02	3.98 ± 0.02	11.53 ± 0.02	11.29 ± 0.02

[a] This work.
[b] Ref. [11].
[c] Ref. [12].

In the first part, the transfer enthalpies are positive and increase with increasing surfactant concentration. The positive values of $\Delta_{tr}H_m$ can be interpreted as due to the release of structured water molecules from the hydration co-spheres into the bulk. Partial dehydration of amino acid or surfactant molecules is an endothermic process. $\Delta_{tr}H_m$ does not difference significantly among the amino acids. The hydration shells of ammonium and carboxylate groups are large enough to overlap the side chains of amino acid molecules and the charged groups strongly disrupt the structure of water up to a considerable distance [23]. Therefore, amino acids with the same charged terminals (COO^- and NH_3^+) leads to almost the same values of $\Delta_{tr}H_m$ at these surfactant concentrations.

In the second part, the values of the transfer enthalpies decrease with increasing concentration of surfactant. In this concentration range, the amino acid molecules mainly interact with the ion head groups of the micelles. Two main kinds of ion–ion interactions: (a) between SO_4^{2-} of SDS or Br^- of DTAB and the NH_3^+ group of amino acids, and (b) between Na^+ of SDS or N^+–$(CH_3)_3$ group of DTAB and the COO^- group of amino acids, make exothermic contributions to the transfer enthalpies and play more important roles as the concentration of surfactant increases. As the size of side chain groups of amino acid molecules increases, the ion–ion interactions become weaker and weaker. As a result, the transfer enthalpies of glycine have the most negative values and those of threonine have the most positive values.

In the third part, amino acid molecules insert into the micelles and interact with the hydrophobic tails of the surfactant molecules. There are three kinds of factors in this part: (a) ion–hydrophobic interactions between zwitterions of amino acid molecules and alkyl chain of surfactant molecules; (b) hydrophilic–hydrophobic interactions between hydrophilic side

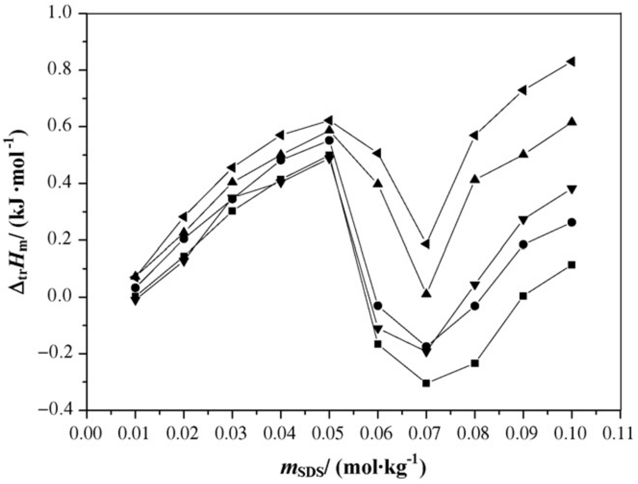

Fig. 1. Enthalpies of transfer of amino acids from water to aqueous SDS solutions at 298.15 K: (■) glycine; (●) alanine; (▲) valine; (▼) serine; (◄) threonine.

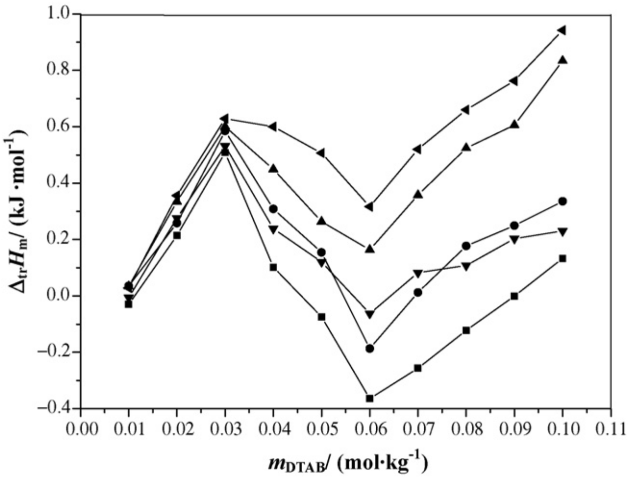

Fig. 2. Enthalpies of transfer of amino acids from water to aqueous DTAB solutions at 298.15 K: (■) glycine; (●) alanine; (▲) valine; (▼) serine; (◄) threonine.

chain of amino acid molecules and hydrophobic chain of surfactant molecules; (c) hydrophobic–hydrophobic interactions between hydrophobic side chain of amino acid molecules and ethylene tail of surfactant molecules. According to the hydration co-sphere overlap model [24], these three types of interactions are endothermic. Therefore, the transfer enthalpies increase again with increasing surfactant concentration, in the order threonine > valine > alanine ≈ serine > glycine, which has a good correlation with the size of side chain.

Acknowledgements

The authors are grateful for the financial supports from the National Natural Science Foundation of China (no. 20673098) and the Natural Science Foundation of Zhejiang Province, China (no. M203090).

References

[1] L. Zhou, C.L. Liu, L. Ma, R.S. Lin, Thermochim. Acta 468 (2008) 116–118.
[2] C.L. Liu, L. Zhou, R.S. Lin, J. Solution Chem. 36 (2007) 923–937.
[3] X. Wang, R. Zhang, L. Xu, R.S. Lin, J. Mol. Liq. 133 (2007) 111–115.
[4] L. Ma, N. Xu, G.M. Lin, R.S. Lin, Thermochim. Acta 432 (2005) 20–22.
[5] X. Wang, L. Xu, R.S. Lin, D.Z. Sun, Thermochim. Acta 425 (2005) 31–37.
[6] C.L. Liu, R.S. Lin, Thermochim. Acta 440 (2006) 57–59.
[7] C.L. Liu, R.S. Lin, N. Xu, J. Chem. Eng. Data 50 (2005) 2094–2096.
[8] Y. Lou, R.S. Lin, Thermochim. Acta 316 (1998) 145–148.
[9] L. Xu, X. Wang, R.S. Lin, D.Z. Sun, J. Chem. Thermodyn. 37 (2005) 371–375.
[10] B. Pałecz, Thermochim. Acta 435 (2005) 99–101.
[11] B. Pałecz, J. Therm. Anal. Calorim. 54 (1998) 265–269.
[12] B. Pałecz, Amino Acids 27 (2004) 299–303.
[13] C. Carnero Ruiz, J.A. Molina-Bolívar, J. Aguiar, J.M. Peula-García, Colloids Surf. A 249 (2004) 35–39.
[14] A. Bonincontro, G. Briganti, A. D'Aprano, C. La Mesa, B. Sesta, Langmuir 12 (1996) 3206–3210.
[15] S.K. Singh, A. Kundu, N. Kishore, J. Chem. Thermodyn. 36 (2004) 7–16.
[16] A.K. Rakshit, B. Sharma, Colloid Polym. Sci. 281 (2003) 45–51.
[17] A. D'Aprano, C. La Mesa, N. Proietti, B. Sesta, S. Tatone, J. Solution Chem. 23 (1994) 1331–1346.
[18] S.K. Singh, N. Kishore, J. Solution Chem. 11 (2004) 1411–1427.
[19] A. Ali, S. Sabir, Shahjahan, S. Hyder, Acta Physico-Chim. Sin. 23 (2007) 1007–1012.
[20] L. Yu, T. Lu, Y.X. Luan, J. Liu, G.Y. Xu, Colloids Surf. A 257–258 (2005) 375–379.
[21] S. Paula, W. Sus, J. Tuchtenhagen, A. Blume, J. Phys. Chem. 99 (1995) 11742–11751.
[22] G.Y. Bai, J.B. Wang, H.K. Yan, J. Phys. Chem. B 105 (2001) 9576–9580.
[23] M. Ide, Y. Maeda, H. Kitano, J. Phys. Chem. B 101 (1997) 7022–7026.
[24] H.L. Friedam, C.V. Krishnan, J. Solution Chem. 2 (1973) 119–140.