ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2018, Vol. 92, No. 3, pp. 466–469. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © I.N. Mezhevoi, V.G. Badelin, E.Yu. Tyunina, S.V. Kamkina, 2018, published in Zhurnal Fizicheskoi Khimii, 2018, Vol. 92, No. 3, pp. 399–402.

PHYSICAL CHEMISTRY OF SOLUTIONS

Effect of Tryptophan and Asparagine Structure on the Enthalpic Characteristics of Their Dissolution in Aqueous Solutions of Sodium Dodecyl Sulfate

I. N. Mezhevoi[a,*], V. G. Badelin[a], E. Yu. Tyunina[a], and S. V. Kamkina[b]

[a] *Krestov Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, 153045 Russia*
[b] *Ivanovo State University of Chemistry and Technology, Ivanovo, 153000 Russia*
**e-mail: inm@isc-ras.ru*

Received May 3, 2017

Abstract—The integral enthalpies of dissolution of L-tryptophan and L-asparagine in aqueous solutions of sodium dodecyl sulfate (surfactant) at surfactant concentrations of up to 0.05 mol/kg of the solvent are determined and estimated calorimetrically. Standard values of the enthalpies of dissolution and transfer of amino acids from water to a mixed solvent are calculated. The calculated enthalpy coefficients of pair interactions between amino acids and surfactant molecules have positive values. Hydrophobic interactions between amino acids and surfactants have the dominant effect on the enthalpy characteristics of the interaction in a three-component solution.

Keywords: enthalpy of dissolution, amino acid, sodium dodecyl sulfate, hydrophobic interaction, aqueous solution

DOI: 10.1134/S0036024418030202

INTRODUCTION

Model compounds (amino acids, peptides) and detergents, both ionic and neutral, are widely used in protein research. Ionic detergents (substances containing a hydrophobic hydrocarbon radical and a hydrophilic functional group) are effective denaturants. Sodium dodecyl sulfate, an anionic surfactant, is an excellent example of a denaturant. Denaturation is normally accompanied by a loss of specific functions of proteins, which explains the interest in studying the mechanisms of protein denaturation [1, 2]. This property is very often used to isolate proteins and purify biological lipid membranes [3]. In ionic surfactants, the electrostatic forces between polar charged groups of the ionic unit of sodium dodecyl sulfate are repulsive, and the hydrophobic interactions of the nonpolar unit of the surfactant are the preferential attractive moving forces [4–6]. The main factors in the association of protein compounds and ionic surfactants are thus electrostatic and hydrophobic interactions.

EXPERIMENTAL

The integral enthalpies of dissolution of amino acids were measured using a variable temperature calorimeter with isothermal jacket. The calorimeter design, the operating procedure, and the assessment of the accuracy and reliability of measuring the enthalpy of dissolution were described in detail in [7].

The concentration of amino acids varied in the range of 0.004–0.006 mol/kg. The enthalpy of dissolution ($\Delta_{sol}H^m$) of biomolecules in the studied concentration range (up to 0.006 mol/kg) did not depend on the concentration of amino acids, so the arithmetic means of the thermal dissolution effects ($\Delta_{sol}H^m$) after 2–3 measurements were taken as the standard values of $\Delta_{sol}H^0$. L-Tryptophan (Sigma-Aldrich, >98%) and L-asparagine (Sigma-Aldrich, ≥99%) were recrystallized from water–ethanol mixtures and dried under vacuum at 343 K for 48 h before each experiment. The water for preparing the solutions was twice distilled (specific conductivity, 10^{-5} Ω^{-1} cm^{-1}). Sodium dodecyl sulfate (Sigma-Aldrich, ≥99%) was used without further purification.

RESULTS AND DISCUSSION

Experimental data on $\Delta_{sol}H^0$ of L-tryptophan (Trp) and L-asparagine (Asn) in mixed solutions of water with sodium dodecyl sulfate (SDS) are presented in Table 1. The dependences of the enthalpies of transfer ($\Delta_{tr}H^0$) of amino acids from water to the SDS aqueous solution studied in this work and in [8] on its mole fraction (X_2) are given in Fig. 1.

Table 1. Standard enthalpies of dissolution ($\Delta_{sol}H^0$, kJ/mol) of L-tryptophan and L-asparagine in water–SDS solutions at 298.15 K

L-tryptophan		L-asparagine	
m_y	$\Delta_{sol}H^0$	m_y	$\Delta_{sol}H^0$
0.001	12.74 ± 0.06	0.001	22.58 ± 0.10
0.003	12.77 ± 0.06	0.003	22.59 ± 0.10
0.006	12.82 ± 0.06	0.006	22.61 ± 0.10
0.008	12.86 ± 0.06	0.008	22.63 ± 0.10
0.010	12.89 ± 0.06	0.010	22.64 ± 0.10
0.020	12.98 ± 0.06	0.020	22.66 ± 0.10
0.030	13.04 ± 0.06	0.030	22.57 ± 0.10
0.040	13.08 ± 0.06	0.040	22.35 ± 0.10
0.050	13.07 ± 0.06	0.050	22.01 ± 0.10

Molality of SDS (mol kg^{-1}).

The obtained enthalpies of amino acid transfer had positive values and grew along with the concentration of the surfactant for L-tryptophan. This resulted from the overlapping of the hydration shells of molecules of the investigated substances and the destruction of hydrogen bonds between water molecules and carboxyl, and the amino groups of amino acids, when they interacted with SDS, which led to the dehydration of the interacting substances in a three-component solution. With L-asparagine, a drop in the enthalpies of biomolecule transfer was observed at SDS mole fraction >0.0003, due possibly to an increase in the electrostatic and donor-acceptor interactions between the side and terminal groups of the amino acid and the hydrophilic part of the SDS molecules. Note that with amino acids, the increase in SDS concentration reduced the enthalpies of transfer, which could also be due to an increase in the number of interactions with the hydrophilic part of the amphiphilic SDS. The enthalpies of transfer were determined from the different contributions with opposite charges from different concurrent interactions in the solution and solvation processes. To analyze the observed graphical dependences, we used an approach based on interpreting the interaction between amino acids and a component dissolved in water, which has proved to be effective among different researchers [9–11].

In three-component amino acid–surfactant–water systems, the molecules of hydrated solutes are located at the distances of short- and long-range interactions. As a result, the hydrate shells of molecules overlap in the investigated system, which alters the physicochemical parameters characterizing the interparticle molecular interaction in the solution. The enthalpies of amino acid transfer calculated in this work were determined by the sum of thermodynamic contributions with opposite charges. Thermochemical changes occurring in a multicomponent system can be described by a simple equation of enthalpy contribu-

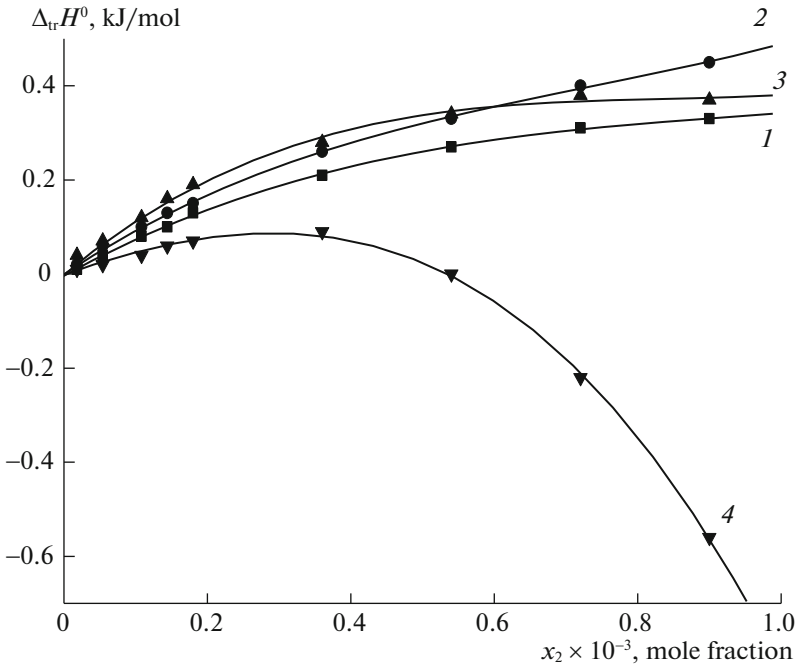

Fig. 1. Dependences of enthalpies of transfer $\Delta_{tr}H^0$ of (*1*) glycine [8], (*2*) L-cysteine [8], (*3*) L-tryptophan, and (*4*) L-asparagine from water to SDS-water mixtures on SDS mole fraction X_2 at 298.15 K.

tions to the thermodynamics of the dissolution of amino acids:

$$\Delta_{tr}H^0 = -\Delta H_1 - \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5, \quad (1)$$

where ΔH_1 denotes bipolar ion interactions between the polar centers of amino acids (carboxyl, carbonyl, amino groups) and the $-OSO_3^-$ and Na^+ units of SDS; ΔH_2 represents donor–acceptor interactions caused by the O=C–NH_2 side group of L-asparagine and the oxygen atoms of the hydrophilic unit of SDS; ΔH_3 is for hydrophobic ion interactions between the zwitterions of amino acid molecules (dipeptide) and the lipophilic groups of the SDS surfactant; ΔH_4 denotes hydrophilic–hydrophobic interactions between the hydrophilic side chain of amino acids molecules and the hydrophobic part of SDS molecules; and ΔH_5 represents hydrophobic–hydrophobic interactions between hydrophobic amino acid groups and the ethylene moiety of SDS molecules.

The first and second types of interactions made a negative contribution, while the third, fourth, and fifth ones, which predominate throughout the range of surfactant concentrations, made positive contributions to the $\Delta_{tr}H^0$ of amino acid transfer from water to the SDS aqueous solution. To quantify the interparticle interactions in aqueous solutions, we performed a regression analysis using the McMillan–Mayer theory [12] by calculating the enthalpy coefficients of pair interactions (h_{xy}) of biomolecules with SDS. The concentration dependences of $\Delta_{sol}H^0 = f(m_y)$ of amino acids in SDS aqueous solutions were processed using a third degree polynomial:

$$\Delta_{sol}H^0 = a_0 + a_1 m_y + a_2 m_y^2 + a_3 m_y^3, \quad (2)$$

where m_y is the SDS molal concentration; a_0, a_1, a_2, a_3 are approximation coefficients, calculated according to the least squares method.

As a result of our regression analysis, equations were obtained for L-tryptophan and L-asparagine in SDS aqueous solutions, respectively:

$$\Delta_{sol}H^0 = (12.70 \pm 0.01) + (19.20 \pm 1.18)m_y - \ldots, \quad R = 0.998, \quad SD = 0.008, \quad N = 9; \quad (3)$$

$$\Delta_{sol}H^0 = (22.56 \pm 0.01) + (10.95 \pm 1.01)m_y - \ldots, \quad R = 0.999, \quad SD = 0.004, \quad N = 9. \quad (4)$$

The values of the free terms of Eqs. (3), (4) correspond to the standard enthalpies of dissolution of L-tryptophan and L-asparagine in pure water, which are in good agreement with our earlier determined and literature values. For example, $\Delta_{sol}H^0$(Trp) = 12.36 ± 0.03 [13], $\Delta_{sol}H^0$(Trp) = 12.70 ± 0.06 [14], $\Delta_{sol}H^0$(Asn)=20.95 ± 0.14 [13], $\Delta_{sol}H^0$(Asn) = 24.06 [15], $\Delta_{sol}H^0$(Asn) = 22.57 ± 0.10 [16]. The enthalpy coefficients of pair interactions (h_{xy}) were calculated using the equation $h_{xy} = a_1/2$ [17]. The values obtained for amino acids in SDS aqueous solutions are given in Table 2.

Table 2. Enthalpy coefficients of pair interactions (h_{xy}, kJ kg mol^{-2}) of amino acids with SDS in aqueous solutions at 298.15 K

Glycine	L-cysteine	L-tryptophan	L-asparagine
7.54 ± 0.34 [8]	8.49 ± 0.44 [8]	9.60 ± 0.59	5.48 ± 0.36

All of the calculated coefficients and the h_{xy} obtained in [8] had positive values in water–mixed solvents. This means the endothermic processes associated with the structural rearrangement of the three-component solution and the release of water molecules from the hydrate shells of amino acids and SDS predominate over direct interactions of the solvated polar groups of interacting molecules.

Coefficients h_{xy} of the amino acids fell in the Trp > Cys > Gly > Asn series. Hydrophobic interactions characterize the process of molecular association by nonpolar substances or nonpolar units of amphiphilic compounds in aqueous solutions. Different electrostatic interactions and hydrogen bonds in three-component systems also promote hydrophobic interactions, which raises the endothermicity of dissolution [18]. Replacing the hydrogen atom in the glycine molecule with the hydrophobic–hydrophilic CH_2-SH group in cysteine raises the enthalpy coefficient of interaction with SDS, which also testifies to the dominance of hydrophobic effects in the investigated range of concentrations and the structural reorganization of the three-component system. The presence of benzene and indole rings in tryptophan classifies it as a group of classical hydrophobic amino acids, which is reflected in the highest h_{xy} at interaction with SDS. The lowest enthalpy coefficient of pair interaction for Asn is determined by the presence of an additional center of specific solvation O=C–NH_2 in it, which raises the exothermicity of dissolution due to direct interactions with the hydrophilic unit of SDS.

A linear dependence of enthalpy pair interaction coefficients (h_{xy}) of amino acids with SDS on the hydrophobicity parameters of biomolecules (g) was calculated in [19]: $h_{xy} = (7.98 \pm 0.56) + (0.19 \pm 0.08)g$. There is an increase in the enthalpy pair interaction coefficients (h_{xy}) of amino acids with SDS as hydrophobicity falls in the Trp > Cys > Gly > Asn series, which testifies to the predominance of hydrophobic effects in the investigated range of concentrations, processes of association of alkyl nonpolar side chains of biomolecules with the SDS solvophobic unit, and an entropy component in the thermodynamics of the dissolution of biomolecules in a surfactant solution.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 15-43-03003-r_tsentr_a.

REFERENCES

1. M. Bello, G. Gutierrez, and E. Garcia-Hernandez, Biophys. Chem. **165–166,** 79 (2012).
2. I. N. Mezhevoi and V. G. Badelin, Russ. J. Phys. Chem. A **87**, 2023 (2013).
3. M. S. Hossain, T. K. Biswas, D. Ch. Kabiraz, Md. N. Islam, and M. E. Huque, J. Chem. Thermodyn. **71**, 6 (2014).
4. A. L. Lehninger, D. L. Nelson, and M. M. Cox, *Principles of Biochemistry* (Worth, USA, 1993).
5. S. K. Singh and N. J. Kishore, Phys. Chem. B **110**, 9728 (2006).
6. I. N. Mezhevoi, V. G. Badelin, and E. Yu. Tyunina, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol. **58** (8), 33 (2015).
7. V. G. Badelin, E. Yu. Tyunina, and I. N. Mezhevoi, Russ. J. Appl. Chem. **80**, 711 (2007).
8. V. G. Badelin, I. N. Mezhevoi, and E. Yu. Tyunina, Russ. J. Phys. Chem. A **91**, 521 (2017).
9. T. H. Lilley, Pure Appl. Chem. **65**, 2551 (1993).
10. T. H. Lilley, E. Moses, and I. R. Tasker, J. Chem. Soc., Faraday Trans. **76**, 906 (1980).
11. I. N. Mezhevoi and V. G. Badelin, Russ. J. Phys. Chem. A **89**, 2222 (2015).
12. W. G. McMillan and J. E. Mayer, J. Chem. Phys. **13**, 276 (1945).
13. M. Abu-Hamdlyyah and A. Shehabuddin, J. Chem. Eng. Data **27**, 74 (1982).
14. B. Palecz, J. Am. Chem. Soc. **127**, 17768 (2005).
15. C. A. Zittle and C. L. A. Schmidt, J. Biol. Chem. **108**, 161 (1935).
16. I. N. Mezhevoi and V. G. Badelin, Russ. Chem. Bull. **57**, 2452 (2008).
17. J. E. Desnoyers, G. Perron, L. Avedikian, and J.-P. Morel, J. Solution Chem. **5**, 631 (1976).
18. G. Castronuovo, V. Elia, C. Giancola, and S. Puzziello, J. Solution Chem. **19**, 855 (1990).
19. J. M. R. Parker, D. Guo, and R. S. Hodges, Biochemistry **25**, 5425 (1986).

Translated by E. Stepanova