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Short communication

Volumetric properties of amino acids in aqueous solution of nonionic surfactant

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ABSTRACT

The volumetric properties of amino acids (DL-glycine, DL-alanine, DL-serine, L-aspartic acid, L-lysine, and L-leucine) in aqueous solution of nonionic surfactant hexadecyl poly[oxyethylene(25)] alcohol ($C_{16}A_{25}$) are studied. The values of apparent molar volumes V_ϕ, partial molar volumes $V^0_{2,m}$ and volumes of transfer $\Delta_{t_2}V^0_{2,m}$ are calculated. The changes of volumes of transfer are discussed in terms of hydrophilic–hydrophobic interactions. The linear correlation of $V^0_{2,m}$ for a amino acids is utilized to calculate the contribution of the charge groups (NH_3^+, COO^-), CH_2 group and other alkyl chains of amino acids to $V^0_{2,m}$.

1. Introduction

Interactions of proteins with their surrounding environment play an important role in their conformational characteristics. The most important of those are between solute and solvent molecules [1]. The study of these interactions provides important insight into the conformational stability and folding/unfolding behavior of globular proteins [2]. Because proteins are large complex molecules, a direct study of protein–electrolyte interactions is difficult. It is therefore useful to investigate the solution behavior of compounds model such as amino acids, peptides and their derivatives that constitute part of the protein structures [3–6].

Surfactants are largely employed in pharmaceutical [7,8] and biological [9,10] processes. In technological perspectives surfactant–protein interactions are very important because they regular the functional properties of proteins. Surfactant–amino acids interactions are largely studied in literature using conductivity [11,12], chromatography [11], circular dichroism [13], fluorescence [14,15] and direct calorimetry [16,17]. Interactions surfactants with proteins may lead to some changes of configurations and molecular characteristics of globular proteins. However, some details in the model of interactions of surfactants with proteins still remain unanswered. Therefore, it is very important to understand theory and the nature of surfactant–amino acid interactions both as qualitive and quantitative.

The survey of the literature shows that the volumetric properties of amino acids are largely reported [2–6,18–33]. Although this many problems are not completely described yet.

In this paper the results of investigation of volumetric properties for system nonionic surfactant $C_{16}A_{25}$–amino acid–water are reported and the volumes of transfer of amino acids from water to water solution of $C_{16}A_{25}$ are calculated. This parameter is discussed in terms of various interactions occurring in these solutions.

2. Experimental

Nonionic surfactant hexadecyl poly[oxyethylene(25)] alcohol ($C_{16}A_{25}$ – $C_{16}H_{33}O(C_2H_4O)_{25}H$) (Shebekino, Russia) was purified according [34]. The containing of pure substance in perfected samples is no less than 98%. Amino acids (DL-glycine, DL-alanine, DL-serine, L-aspartic acid, L-lysine and L-leucine) were synthesized in Biotechnology Institute of Armenia and used without further purification (>99.8%).

Densities of solutions were measured using a vibrating-tube digital densimeter DMA-4500 (Anton Paar, Austria) with precision of $\pm(5\times10^{-5})\,\mathrm{g\,cm^{-3}}$. The solutions were thermostated with precision of ±0.01 K. The densimeter was calibrated with dry air and pure water under atmospheric pressure.

3. Results and discussion

The densities ρ of system $C_{16}A_{25}$–amino acid–water in pre-micellar ($5\times10^{-5}\,\mathrm{mol\,l^{-1}}$) and post-micellar ($5\times10^{-4}\,\mathrm{mol\,l^{-1}}$) regions at 303 and 333 K are determined. The effect of amino acids

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Table 1

Densities ρ and apparent molar volumes V_ϕ of system surfactant–amino acid–water by dependence on amino acid concentration.

m (mol kg^{-1})	T = 303 K		T = 333 K	
	ρ (g cm^{-3})	V_ϕ (cm^3 mol^{-1})	ρ (g cm^{-3})	V_ϕ (cm^3 mol^{-1})
[$C_{16}A_{25}$] = 5 × 10^{-5} mol l^{-1}				
Glycine				
0.00000	0.99565	–	0.98319	–
0.00106	0.99568	46.77672	0.98322	47.00293
0.00216	0.99571	47.30379	0.98325	47.54366
0.00574	0.99579	50.71671	0.98334	49.24117
0.01304	0.99587	58.29589	0.98348	53.26036
0.04818	0.99582	71.75609	0.98351	69.38897
Alanine				
0.00077	0.99567	63.17748	0.98321	63.65058
0.00161	0.99568	70.75317	0.98322	71.24334
0.00346	0.99569	77.72380	0.98324	75.56859
0.00562	0.99566	87.59302	0.98322	84.99690
0.00817	0.99559	96.77070	0.98316	94.32315
Serine				
0.00150	0.99571	65.10454	0.98326	58.51500
0.00250	0.99574	69.13724	0.98329	65.40909
0.00300	0.99575	71.82630	0.98330	68.85633
0.00400	0.99578	72.66465	0.98332	73.16472
Aspartic acid				
0.00188	0.99578	63.81827	0.98332	63.73184
0.00752	0.99614	67.81752	0.98369	66.45777
0.00940	0.99626	68.07748	0.98375	66.99958
0.01222	0.99642	69.96372	0.98399	67.49484
0.01598	0.99663	71.64686	0.98422	68.52371
0.01880	0.99677	73.40234	0.98439	69.45845
Lysine				
0.00036	0.99568	62.57290	0.98322	62.28706
0.00069	0.99570	73.53584	0.98325	63.56157
0.00138	0.99574	80.84206	0.98330	66.02971
0.00207	0.99575	93.02215	0.98335	68.52473
0.00276	0.99578	99.11101	0.98340	69.77034
Leucine				
0.00030	0.99567	64.32058	0.98317	64.27526
0.00052	0.99568	73.37260	0.98322	66.92442
0.00103	0.99570	82.59940	0.98325	72.97392
0.00180	0.99572	92.33641	0.98327	87.25546
[$C_{16}A_{25}$] = 5 × 10^{-4} mol l^{-1}				
Glycine				
0.00000	0.99572	–	0.98326	–
0.00154	0.99577	42.57298	0.98331	42.69224
0.00872	0.99600	42.92358	0.98353	44.23815
0.02095	0.99639	43.03699	0.98390	44.64984
0.03082	0.99670	43.20838	0.98419	45.02287
Alanine				
0.00161	0.99577	58.05619	0.98332	51.96555
0.00346	0.99580	66.05667	0.98337	57.62514
0.00562	0.99584	67.83811	0.98341	62.89870
0.00817	0.99586	72.08893	0.98346	65.18153
Serine				
0.00100	0.99576	65.10411	0.98331	55.06782
0.00200	0.99579	70.14492	0.98334	65.40871
0.00300	0.99581	75.18908	0.98335	75.75050
0.00400	0.99581	82.75010	0.98334	86.09382
Aspartic acid				
0.00188	0.99585	63.81868	0.98339	63.73240
0.00376	0.99597	66.49281	0.98351	66.47483
0.00752	0.99621	67.81737	0.98374	69.20884
0.00940	0.99633	68.07729	0.98385	70.30081
0.01222	0.99650	69.13783	0.98401	71.72722
0.01598	0.99672	70.38365	0.98421	73.70232
0.01880	0.99687	71.78785	0.98434	75.76159
Lysine				
0.00050	0.99576	65.93570	0.98330	65.73579
0.00100	0.99580	65.93305	0.98334	65.73311
0.00250	0.99592	65.92510	0.98346	65.72425
0.00300	0.99596	62.92246	0.98350	65.72242
0.00400	0.99604	65.91716	0.98358	65.71707
Leucine				
0.00317	0.99593	64.73265	0.98347	64.69553
0.00871	0.99624	71.31001	0.98370	80.94267
0.02092	0.99674	82.30156	0.98405	94.09500
0.03614	0.99671	103.83038	0.98430	103.3558

The maximum uncertainty in the V_ϕ values is estimated to be not more than ±(5 × 10^{-5}) cm^3 mol^{-1}.

on cmc of $C_{16}A_{25}$ has been studied by us earlier [12] and it has been shown that with increased of amino acids concentration the cmc of $C_{16}A_{25}$ decreases. Thus, the concentrations of surfactant are chosen in view of the influence of amino acids on micellization behavior of $C_{16}A_{25}$ and in the case of 5×10^{-5} mol l^{-1} concentration the surfactant is only in the form of molecules and in the case of 5×10^{-4} mol l^{-1} concentration surfactant molecules are in the form of micelles.

Based on values of densities the apparent molar volumes V_ϕ are calculated by the relation:

$$V_\phi = \frac{1000(\rho_0 - \rho)}{m\rho\rho_0} + \frac{M}{\rho} \tag{1}$$

where M and m are the molar mass and molality of solute, respectively, ρ and ρ_0 are the densities of solution and solvent, respectively. The values of densities and apparent molar volumes are given in Table 1.

In all cases the standard partial molar volumes ($V^0_{2,m}$) are obtained by least-squares fitting to the following equation [35]:

$$V_\phi = V^0_{2,m} + S_v \cdot m \tag{2}$$

where S_v is the experimental slope, which sometimes is considered with coefficient of volumetric pairwise interaction [36,37]. The values of standard partial molar volumes are given in Table 2. The values of $V^0_{2,m}$ are positive in all cases and show a linear variation with number of carbon atoms in the alkyl chain of amino acids. That linear variation is represented by relation [6,27,32,35,38,39]:

$$V^0_{2,m} = V^0_2(\mathrm{NH_3^+}, \mathrm{COO^-}) + n_C V^0_2(\mathrm{CH_2}) \tag{3}$$

where n_C is the number of carbon atoms in the alkyl chain of amino acids, $V^0_2(\mathrm{NH_3^+}, \mathrm{COO^-})$ and $V^0_2(\mathrm{CH_2})$ are the zwitterionic end groups and the methylene group contribution to $V^0_{2,m}$, respectively. The values of $V^0_2(\mathrm{NH_3^+}, \mathrm{COO^-})$ and $V^0_2(\mathrm{CH_2})$ are given in Table 3. But as the amino acids studied in this paper contain CH_2–(glycine), CH_2CH_2–(alanine), CH_2CH–(serine), $(CH_2)_4CH$–(lysine), $(CH_3)_2CH_2(CH)_2$–(leucine) groups too, from values of $V^0_2(\mathrm{CH_2})$ the contribution of CH– and CH_3– groups are calculated. As suggested by Hakin et al. [40,41], the contribution of the other alkyl chain of the amino acids are calculated as follows:

$$V^0_2(\mathrm{CH_3}) = 1.5\ V^0_2(\mathrm{CH_2}) \tag{4}$$

$$V^0_2(\mathrm{CH}) = 0.5\ V^0_2(\mathrm{CH_2}) \tag{5}$$

and reported in Table 3. As shown in Table 3, the values of V^0_2 ($\mathrm{NH_3}^+$, $\mathrm{COO^-}$) are higher than V^0_2 ($\mathrm{CH_2}$), which indicates that interactions between zwitterionic groups and molecules (micelles) of $C_{16}A_{25}$ are stronger than hydrophobic interactions between alkyl groups and molecules (micelles) of $C_{16}A_{25}$ [32].

Table 2
Standard partial molar volumes for amino acid–water system and $C_{16}A_{25}$–amino acid–water system in pre-micellar and in post-micellar regions at 303 and 333 K.

Amino acids	$V_{2,m}^0$ (cm^3 mol^{-1})	
	T = 303 K	T = 333 K
In water		
Glycine	43.12641	44.23920
Alanine	60.29334	61.83557
Serine	64.34091	54.19354
Aspartic acid	64.98372	64.00313
Lysine	62.21447	62.83972
Leucine	62.78911	63.11389
$[C_{16}A_{25}] = 5 \times 10^{-5}$ mol l^{-1}		
Glycine	43.87221	45.62730
Alanine	61.99948	62.52119
Serine	64.03160	44.72528
Aspartic acid	63.61896	63.69733
Lysine	61.02780	61.42771
Leucine	62.40585	63.06212
$[C_{16}A_{25}] = 5 \times 10^{-4}$ mol l^{-1}		
Glycine	42.63240	42.71380
Alanine	58.49105	52.49946
Serine	64.58931	53.93217
Aspartic acid	64.14729	63.57344
Lysine	65.93835	65.73955
Leucine	60.45170	63.65637

Based on values of standard partial molar volumes the volumes of transfer $\Delta_{t_2}V_2^0$ for the amino acids from water to aqueous solution of surfactant are calculated by relation (6) [4]:

$$\Delta_{t_2}V_2^0[\text{from water to aqueous solution of surfactant}] = V_{2,m}^0[\text{in aqueous solution of surfactant}] - V_{2,m}^0[\text{in water}] \quad (6)$$

The values of $V_{2,m}^0$ [in water] are determined by us and reported in Table 2. We must note that values of $V_{2,m}^0$ [in water] for amino acids agree well with reference data [32,42].

As the influence of amino acids on properties of nonionic surfactant is studied electrostatic interactions among components of system are excluded. In general, there can occur only (1) hydrophobic–hydrophobic interactions between alkyl chain of surfactant and hydrophobic groups of amino acids, (2) hydrophilic–hydrophilic interactions and (3) ion–hydrophilic interactions between the charge centers (NH_3^+, COO^-) of amino acids and hydrophilic (polyoxyethylene) part of $C_{16}A_{25}$. The hydrophilic–hydrophilic and ion–hydrophilic interactions would lead to the positive volumes of transfer, since there is an increase in the electrostriction effect and overall water structure destructed. The hydrophobic–hydrophobic interactions would lead to negative values of volumes of transfer, because of the reduction of water structure that is formed around those groups as a result of the cosphere overlap as it was developed by Frank and Evans [1,43]. From dates in Table 4 follow that in case of neutral glycine, alanine and acidic aspartic acid the values of $\Delta_{t_2}V_2^0$ in pre-micellar region are positive, while in post-micellar region these values are negative. This means, that in presence of these amino acids in pre-micellar region the hydrophilic–hydrophilic and ion–hydrophilic interactions are dominant, while in post-micellar region the hydrophobic–hydrophobic interactions are dominant. We must note, that the negative values of $\Delta_{t_2}V_2^0$ for glycine in aqueous solutions of nonionic surfactant at high temperatures have been obtained earlier by other authors too [27,28]. Among studied neutral amino acids in case of serine the values of $\Delta_{t_2}V_2^0$ are always negative. We suggest that this is because of existing of polar hydrophobic –OH group in molecule of serine. At the same time for neutral leucine values of $\Delta_{t_2}V_2^0$ are negative in pre-micellar region, while in post-micellar region with increase of temperature values of $\Delta_{t_2}V_2^0$ become positive. We have not full explanation why leucine has a different behavior from other neutral amino acids. In case of basic lysine, as follow from dates in Table 4, in pre-micellar region the hydrophilic–hydrophilic interactions are dominant, while in post-micellar region the hydrophobic–hydrophobic interactions are dominant.

Table 3
Contribution of zwitterionic groups (NH_3^+, COO^-), methylene (CH_2) group and the other alkyl groups to standard partial molar volumes in aqueous solutions of $C_{16}A_{25}$ in pre-micellar and in post-micellar regions.

	V_2^0 (cm^3 mol^{-1})	
	T = 303 K	T = 333 K
$[C_{16}A_{25}] = 5 \times 10^{-5}$ mol l^{-1}		
NH_3^+, COO^-	37.24572	36.20356
CH_2–	17.88955	18.40868
CH_2CH_2–	35.77910	36.81736
CH_2CH–	26.83433	27.61302
$(CH_2)_4CH$	80.50298	82.83906
$(CH_3)_2CH_2(CH)_2$	89.44775	92.04340
$[C_{16}A_{25}] = 5 \times 10^{-4}$ mol l^{-1}		
NH_3^+, COO^-	36.59149	37.10226
CH_2–	18.00438	18.18464
CH_2CH_2–	36.00876	36.36928
CH_2CH–	27.00657	27.27696
$(CH_2)_4CH$	81.01971	81.83088
$(CH_3)_2CH_2(CH)_2$	90.02190	90.92320

Average correlation coefficient: 0.99954.

Table 4
The values of transfer volumes of amino acids from water to aqueous solutions of surfactant for $C_{16}A_{25}$–amino acid–water system.

	$\Delta_{t_2}V_{2,m}^0$ (cm^3 mol^{-1})	
	T = 303 K	T = 333 K
$[C_{16}A_{25}] = 5 \times 10^{-5}$ (mol l^{-1})		
Glycine	0.74580	1.38810
Alanine	1.70614	0.68562
Serine	−0.30931	−1.04974
Aspartic acid	1.36476	0.30580
Lysine	−1.18667	−1.41201
Leucine	−0.38326	−0.05177
$[C_{16}A_{25}] = 5 \times 10^{-4}$ (mol l^{-1})		
Glycine	−0.49401	−1.52540
Alanine	−1.80229	−9.33611
Serine	−0.24840	−9.46826
Aspartic acid	−0.83643	−0.42969
Lysine	3.72388	2.89983
Leucine	−2.33741	0.54248

For the amino acids with different hydrophobic contents we obtained small values of the standard partial molar volumes of transfer from water to surfactant solutions. These results indicate an overall balance in the interactions of zwitterionic/hydrophilic groups of amino acids with the hydrophilic groups of $C_{16}A_{25}$, and of the hydrophobic/ionic/hydrophilic groups of the amino acids with the hydrophobic groups of $C_{16}A_{25}$.

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