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Volumetric and conductometric studies on the interactions of dipeptides with potassium perfluoroalkanesulfonate in aqueous solution at different temperatures

Zhenning Yan *, Xiangli Wen, Yunxia Kang, Shuangyan Zhang, Shuangyan Wu

College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, Henan 450001, PR China

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ABSTRACT

Density and conductivity data for potassium perfluoroalkanesulfonate ((potassium perfluorobutanesulfonate (PFBS) and potassium perfluorooctanesulfonate (PFOS)) + dipeptide + water) systems were determined at different temperatures. The standard partial molar volume ($V^{o}_{2,\phi}$), standard partial molar volume of transfer for dipeptide from water to aqueous potassium perfluoroalkanesulfonate solutions ($\Delta_t V^{o}$), hydration number (N_H), partial molar expansibility (E^{o}_{ϕ}) and Hepler's constant for the dipeptides have been calculated from density data. Electrical conductivity was used to estimate the limiting molar conductivity (Λ_o), Walden product ($\Lambda_o\eta$) and energy of activation of the transfer process (Ea) of potassium perfluoroalkanesulfonate in aqueous dipeptide solutions. Effects of temperature and the hydrocarbon chain length of the dipeptides on the volumetric and conductometric properties were examined. The results have been interpreted in terms of solute–solvent interactions and structural changes in the mixed solutions.

1. Introduction

The application of surfactants in the field of biochemistry has given importance to studies of the nature of the interaction between protein and surface active agents in biological systems and biochemical processes such as biological membranes and protein solubilization [1]. There is one kind of special surfactants, fluorinated surfactants or fluorocarbon surfactants. In fluorinated surfactants, all or most hydrogen atoms in the hydrophobe are replaced by fluorine atoms. The substitution of the larger and highly electronegative fluorine atoms for the smaller hydrogen atoms increases the hydrophobicity of the surfactant and lowers surface tension and critical micelle concentration [2]. Fluorinated surfactants are often used in the formulations of the chemical, biosciences, cosmetic and medical industries [2]. Although there is a great work on the study of the interaction of proteins with surfactants, this is, hydrogenated surfactants [3], an important lack can be observed on characterization of the interactions between proteins and fluorinated surfactants.

However, due to the complex conformational and configurational three-dimensional structures of proteins, a direct study of protein–surfactant interaction is quite difficult. Several details in the mode of these interactions remain unanswered. Therefore it is very important to understand the origin and nature of these interactions both qualitatively and quantitatively. In order to understand the fine details, the interactions of the building blocks of the protein with surfactants must be studied. Small peptides are of interest primarily because they contain more complex structure and more component of protein than amino acids. They are also important biological molecules due to their wide range of applications in drug production, ability to act as hormones and for their role as signal transmittance [4]. The addition of small peptides to the solvent may affect the micellization process of a surfactant as a result of changes in solvent characteristics like hydrogen bond formation capacity, dielectric constant, density, viscosity and degree of ionization [5]. In recent years, there has been a growing interest in the interactions present between peptides and surfactant due to their many applications in biosciences, foods and cosmetics, drug delivery, detergency, and biotechnological processes [3,6]. Although some studies on the interaction of surfactants with small peptide molecules have been reported in literatures [7–9], but to the best of our knowledge, very little is known about the properties of the system containing dipeptides and fluorinated surfactants. Taking these into consideration, we employed simple and promising technique, in particular, conductance and density, to substantiate the interactions present between the anionic fluorinated surfactants (potassium perfluorobutanesulfonate (PFBS)

* Corresponding author.

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and potassium perfluorooctanesulfonate (PFOS)) with dipeptides (glycylglycine, glycyl-L-valine, glycyl-L-leucine, glycyl-L-glutamine and L-alanyl-L-glutamine) at different compositions and temperatures. The resulting data have been discussed in terms of the interactions operating in (potassium perfluoroalkanesulfonate + dipeptide + H_2O) systems.

2. Experimental section

2.1. Chemicals

All of the reagents used in this study were purchased from Sigma-Aldrich Shanghai Trading Co. Ltd. Three glycyl dipeptides 2-[(2-aminoacetyl)amino]acetic acid (commonly known as glycylglycine), 2-[(2-aminoacetyl)amino]-3-methylbutanoic acid (common name glycyl-L-valine), and (2*S*)-2-[(2-aminoacetyl)amino]-4-methylpentanoic acid (commonly known as glycyl-L-leucine) were twice recrystallized from aqueous ethanol solution. Two glutamine dipeptides (2*S*)-2-[(2-aminoacetyl)amino]-4-acyl butyric acid (common name glycyl-L-glutamine) and (2*S*)-2-[(2-aminopropionyl)amino]-4-acyl butyric acid (common name L-alanyl-L-glutamine) were used as received. All of the dipeptides were dried for 24 h under vacuum at room temperature. Then they were stored over P_2O_5 in a desiccator before use. Potassium chloride was dried for 48 h at $T = 373$ K and was used to calculate the conductance cell constant. The surfactants potassium perfluorobutanesulfonate (PFBS) and potassium perfluorooctanesulfonate (PFOS) were used without further purification. The details of the compounds used in the work are also given in table 1. Water with a conductivity of $(0.8 \text{ to } 1.0) \times 10^{-4}$ S · m^{-1} was obtained by distilling deionized water. The samples were weighed on a Satorius BP 211D or a Shimadzu AY 120 digital balance with the resolution of (0.00001 and 0.0001) g, respectively.

2.2. Apparatus and procedures

The densities of the solutions were measured using a single capillary pycnometer (Pyrex glass) of bulb capacity of 10×10^{-3} dm^3. The pycnometer was calibrated at the experimental temperatures with doubly distilled water. The pycnometer containing the test solution was equilibrated for about 1 h in a water bath with the desired temperatures. Then it was removed from the thermostatic bath, properly dried, and weighed. Sufficient care was taken to avoid any air bubble entrapment. The necessary air buoyancy corrections were taken care off. All density measurements were performed in triplicate or quadruplicate and the standard uncertainty is ±0.0002 g · cm^{-3} for density at 0.65 confidence level. The temperatures of the solutions were maintained to an uncertainty of ±0.01 K in an electronically controlled thermostatic water bath (Model PDC-A, Ningbo Laifu Instrument Factory).

The electrical conductivity data of each sample were collected with a conductivity meter (Model 145A+, Thermo Orion) which operates with AC current of 50 Hz frequency power source, and a conductivity cell (Model 011510, Thermo Orion). The cell constant was initially calibrated by repeated measurements of standard KCl solutions. All measurements were done in a water circulating jacket, and the temperature was controlled within ±0.02 K using a low temperature thermostat (Model DC-2006, Shanghai Hengping Instrument Factory). Each value is the average of the three times and the relative standard uncertainties are 3%. All data were corrected with specific conductivity of the solvent.

3. Results and discussion

3.1. Volumetric property of dipeptide

Experimental density values of five dipeptides in aqueous 0.04 mol · kg^{-1} PFBS and 0.0005 mol · kg^{-1} PFOS solutions are measured at $T = (288.15, 293.15, 298.15 \text{ and } 303.15)$ K and given in tables S1 and S2 of Supplementary Material as a function of molality of dipeptides (m_p) and temperature. The molality of dipeptides (m_p) was ranged from (0.01942 to 0.2502) mol · kg^{-1}. A small concentration of PFOS was used because of its small solubility (9.660×10^{-4} mol · kg^{-1} at $T = 293.15$ K and 1.267×10^{-3} mol · kg^{-1} at $T = 298.15$ K) and the high Krafft point. The Krafft points of the studied potassium perfluoroalkanesulfonate are (46 and 80) °C for PFBS and PFOS, respectively [10]. Our electrical conductivity experiments showed that there are no micelles in aqueous 0.04 mol · kg^{-1} PFBS and 0.0005 mol · kg^{-1} PFSO solutions at the studied temperature range. The aqueous solutions studied here are monomer solutions. Apparent molar volumes were calculated from the densities of the solutions by using equation (1)

$$V_{2,\phi} = M/\rho - (\rho - \rho_0)/(m_p \rho \rho_0), \quad (1)$$

where M is the molar mass of the dipeptides, ρ_0 is the density of solvent, m_p is the molality of the dipeptide in surfactant mixtures. Calculated apparent molar volumes for dipeptides are also listed in tables S1 and S2 of Supplementary Material. It is shown that the $V_{2,\phi}$ values decrease with increasing dipeptide concentration. A good linear correlation between $V_{2,\phi}$ values and molality of dipeptide was observed (figure S1 of Supplementary Material, taking $V_{2,\phi}$ values at $T = 298.15$ K as example). Therefore, the reported apparent molar volume data for the dipeptides were to be adequately presented by the linear equation

$$V_{2,\phi} = V^o_{2,\phi} + S_V m_p, \quad (2)$$

where $V^o_{2,\phi}$ is the infinite dilution apparent molar volume that equals the standard partial molar volume and S_V is an experimentally determined parameter. Values of $V^o_{2,\phi}$ have been evaluated by weighted least-squares regression analysis and are represented in table 2 along with their standard deviations. At infinite dilution, the solute–solute interaction can be negligible, therefore, the standard partial molar volume and its temperature dependence provide

TABLE 1
Specification of chemical samples.

Chemical name	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method
Glycylglycine	S[a]	0.990	Recrystallization	0.992	HPLC[b]
Glycyl-L-valine	S	0.990	Recrystallization	0.995	HPLC[b]
Glycyl-L-leucine	S	0.990	Recrystallization	0.993	HPLC[b]
Glycyl-L-glutamine	S	0.998			HPLC[b]
L-alanyl-L-glutamine	S	0.992			HPLC[b]
Potassium perfluorobutanesulfonate	S	⩾0.990			NMR
Potassium perfluorooctanesulfonate	S	⩾0.990			NMR

[a] Sigma-Aldrich Shanghai Trading Co. Ltd.
[b] High pressure liquid chromatography.