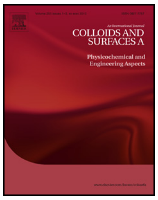
Colloids and Surfaces A: Physicochem. Eng. Aspects 520 (2017) 757–763

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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



Research Paper

The peculiarities of the interphase distribution of amino acids in the cloud point extraction systems

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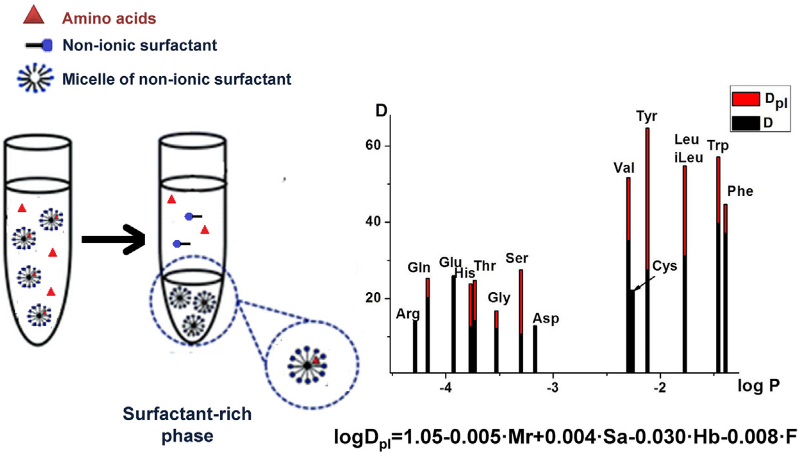
HIGHLIGHTS

- Triton X-100 was used for extraction of a number of L-amino acids.
- The distribution of amino acids in cloud point extraction systems was investigated.
- A number of parameters were chosen for describing amino acids distribution.
- The equation for describing and predicting of distribution coefficient of amino acids was suggested.
- A solvation free Gibbs energy of amino acids was measured.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 December 2016
Received in revised form 14 February 2017
Accepted 15 February 2017
Available online 17 February 2017

Keywords:
Cloud point extraction
Non-ionic surfactant
Distribution coefficient
Amino acids

ABSTRACT

This study presents the particularities of interphase distribution of amino acids between water and non-ionic surfactant-rich phase at cloud point temperature. The influence of a number of hydrophobic/structural parameters of amino acids, such as total hydrophobicity (logP), hydropathy index (Hi), which characterized the nature of amino acid fragment, total molecular surface of amino acids (Sa), their polarity (F), electronegativity of the molecule (X), the maximum possible number of hydrogen bonds, which may form a molecule (Hb), the molecular refraction (Mr), the value of organic (O) and the value of inorganic (I) properties on effectiveness of their cloud point extraction have been studied. Based on obtained data, the equation $\log D = 1.05–0.005\,Mr + 0.004\,Sa–0.030\,Hb–0.008\,F$ has been suggested to describe the interphase transfer of amino acids into surfactant-rich phase. The values of solvation free Gibbs energy for the interphase transfer of amino acids into the surfactant-rich phase were also calculated. The obtained values of free Gibbs energy of amino acids in cloud point extraction system were in the range from -4.4 to $-8.0\,\mathrm{kJ\,mol^{-1}}$. A significant difference between thermodynamic parameters of the cloud point extraction and traditional liquid-liquid extraction with organic solvents is reflected in the ability of surfactant-rich phase extract both hydrophobic and hydrophilic compounds as a consequence of "high organization" and supramolecular nature of this type of phase.

1. Introduction

Cloud point extraction (CPE) is a high-performance, selective and ecologically safe method for microcomponents separation

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http://dx.doi.org/10.1016/j.colsurfa.2017.02.036

and preconcentration [1,2]. Recent publications have indicated the cloud point extraction as an effective procedure for preconcentration and separation of metal ions, organic pollutants and biologically active compounds [3,4]. The efficiency of CPE is provided by its possibility of obtaining high coefficients of absolute preconcentration by analyzing small sample volumes. This method of extraction also provides a decrease of the relative detection limit value owing to absolute preconcentration and an efficient modification of the analyte by a non-ionic surfactant (NS) [5]. The simplicity of combination of cloud point extraction with spectral, atomic absorption, chromatographic and electrochemical analysis allows to use CPE for elaborating the high-sensitive and convenient hybrid analytical methods [6–9]. Especially outstanding results were obtained at the cloud point separation of biomaterials such as proteins, peptides, hormones and viruses [10–12].

It should be noted that the majority of feature articles, concerning the cloud point extraction, are dedicated to the practical usage of this method in analytical and industrial applications. There is significantly less information which contains the theoretical regularities of the substrates distribution and its interphase transfer in the CPE systems. The regularities concerning the extraction of hydrophobic substrates and complexes of metal ions with hydrophobic analytical reagents have been already studied. The influence of the general hydrophobicity and the charge of the molecules on the effectiveness of substrates distribution between the water and the surfactant-rich phase were shown. Based on this data, there were suggested equations to forecast the distribution coefficients of hydrophobic compounds in CPE systems [4,13,14]. On the other hand, there is a lack of information in the literature about the cloud point extraction of hydrophilic compounds.

The solubility of non-ionic surfactants in water is determined by the formation of hydrogen bonds between the oxygen atoms from the polyoxyethylene chains of NS and hydrogen atoms in water molecules. Heating aqueous solutions of non-ionic surfactant causes the destruction of these bonds and provokes phase separation in the system. As a result, two phases are created. The first one is the surfactant-rich phase, formed from large hydrated micelles, and the second one – water phase (aqueous solution phase with the NS concentration approximately as the critical micelle concentration (cmc)) [5].

Surfactant-rich phases are highly organized supramolecular structures [5,15]. Such structures promote the extraction hydrophobic substrates as well as hydrophilic ones. We state that the research of the main factors which may determine the cloud point extraction of hydrophilic substrates creates additional perspectives for the successful application of cloud point extraction for concentration and separation.

The distribution coefficient between water and *n*-octanol (logP) is the main important parameter, which describes the hydrophobic/hydrophilic properties of the substrate. A number of natural L-amino acids under conditions of their existence in zwitterionic forms are characterized with logP values in the range from -4.3 to -1.5. This information allows to define them as highly hydrophilic compounds. Therefore, the aim of our research was to study the influence of the main factors on cloud point extraction of several L-amino acids which were chosen as model hydrophilic substrates. It should be noted that the available in the literature information, concerning about the cloud point extraction of amino acids, contains only optimization of experimental conditions, such as the effect of pH, influence of surfactant and amino acids concentrations, equilibrium temperature and time [12].

Linear solvation free energy relationships (LSERs) have proven to be quite useful for understanding process that describe the transfer of solutes between two condensed phases [16,17]. Recently, Quina [18] have demonstrated that partitioning coefficients (Ks) for incorporation of neutral solutes into detergent micelles in aqueous solution can be presented by equation, which include such parameters as solute hydrogen bond acidity and basicity, dipolarity, polarizability (express as the excess molar refraction of solute) and solute molar volume. Hydrogen bond acidity and basicity of solute are parameters which are calculated on the basis of acidic and basic equilibriums of solute in the solution. These parameters can be calculated for the acids, bases and neutral molecules. It may be significantly more complicated task for calculation of these parameters for the compounds that contain both acidic and basic functional groups and exist in solutions in zwitter-ionic form (for example amino acids). It may limit an application of this method to describe the cloud point extraction of amino acids. Besides, there are many descriptors that describe different physical and chemical properties of amino acid molecules [19,20]. Hence, in the present study we have investigated the physicochemical particularities of interphase distribution of amino acids between water and surfactant-rich phase. We have also studied the effect of a number of hydrophobic and structural parameters on the distribution of amino acids in cloud point extraction system.

2. Materials and methods

2.1. Reagents and apparatus

Triton X-100 (Merck, Darmstadt, Germany) – 4-(1,1,3,3-tetramethylbutyl) phenyl-polyethylene glycol (4-$(C_8H_{17})C_6H_4(OCH_2CH_2)_nOH$, n = 9–10) was used as the non-ionic surfactant. Choice of Triton X-100 (TX-100) was caused by its ability to form phases rapidly during the heating of solutions, compactness of the formed surfactant-rich-phase and its suitable viscosity. Solutions of Triton X-100 were prepared by dissolving of the weighted portion in distilled water. L-Glycine (Gly), L-leucine (Leu), L-isoleucine (iLeu), L-tyrosine (Tyr), L-tryptophan (Trp), L-phenylalanine (Phe), L-serine (Ser), L-threonine (Thr), L-valine (Val), L-cysteine (Cys), L-arginine (Arg), L-histidine (His), L-glutamine (Gln), L-glutamic acid (Glu), L-aspartic acid (Asp), L-methionine (Met) were purchased from Merck (Darmstadt, Germany). Such variety of investigated substrates may exhibit a difference between distribution behaviors for different amino acids groups. Solutions of the amino acids (AA) were prepared by dissolving weighed portions in the aqueous solutions of the non-ionic surfactant. Formaldehyde (Macrochem, Brovary, Ukraine) was used without further purification. Phenolphthalein was obtained from Sigma-Aldrich (St. Louis, MO, USA). Solution of phenolphthalein was prepared by dissolving 100 mg of dye in 10 ml of water-ethanol solution (40:60, v/v). The standardized solution of sodium hydroxide ($0.1\ \mathrm{mol\,l^{-1}}$) was used in study. Ultrapure water was used throughout the experiments and was obtained from a Milli-Q purification system (Millipore, Bedford, MA, USA). pH of the solutions was measured using a pH meter “pH-340” with a glass electrode ESL-43-07.

2.2. Procedure for cloud point extraction

Initial aqueous solutions of nonionic surfactant which contain all required components in calibrated 10 ml cylinders were placed into the water-bath. The temperature of the solutions was controlled by the thermometers immersed in the cylinders and in the water bath. The heating has been performed at the rate of 2.0 °C/min. The cloud point was detected by the appearance of the characteristic opalescence. Solutions were kept at 72 °C for 30 min for equilibration. The density of the surfactant-rich phase was slightly higher than that of the water and the surfactant-rich phase was collected at the bottom of the cylinders without centrifugation.