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Effect of DL-homocysteic acid on W/O microemulsions of potassium naphthenate/1-octanol-*n*-heptane

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Abstract

The effect of DL-homocysteic acid (DL-2-amino-4-sulfonobutyric acid) on W/O microemulsion of potassium naphthenate (80%) and naphthenic acid (20%) in mixed solvent (1-octanol and *n*-heptane) has been found in four phases: (1) Interaction between the amino acid molecules and the polar head groups of the surfactant through hydrogen bonding enhances solubilization in the aqueous cores. (2) The interaction results in the growth of the microemulsion droplets and the homogenization of the particle size distribution. (3) The microstructure of the solubilized water remains unchanged, except that the polarity of the interface is affected. (4) The transition point is reduced to lower water content. A possible mechanism is proposed.

Keywords: DL-Homocysteic acid; Naphthenic acid; Reversed micelles; W/O microemulsion

1. Introduction

Liquid–liquid extraction by an extractant has been considered as a potential technique for the separation of amino acids [1–3]. The formation of reversed micelles and/or W/O microemulsions of the extractant is so closely associated with the separation process that the technique has been represented in terms of "extraction of amino acids or proteins by reversed micelles." Significant interest has been focused on the aggregation behavior of extractants [4–10]. Also, some biologically active materials may be preserved in the aqueous core of the W/O microemulsion droplets instead of by refrigeration [11,12]. The aim of this work is to understand the behavior and the interaction between the biological compound, a peculiar amino acid (DL-homocysteic acid, abbreviated by DLH), and the W/O microemulsion in the mixed organic solvent.

When water is encapsulated into reversed micelles under appropriate conditions, to an extent where the structure of various species involved in the system becomes stable and independent of the water content, the reversed micelle is transferred to W/O microemulsion [4]. In other words, in the W/O microemulsion region, the system is characteristic of its stable state, including the microstructures of the adsorbed film at the interface and the solubilized water, regardless of further changes in aggregate size, water content, and molar fractions of various hydrated water molecules. This feature provides a special and advantageous environment for processing biological materials.

Naphthenic acid is a fraction of crude petroleum and is used as an extractant in the separation of metal ions. It is one of the acid extractants that have received extensive investigation in this laboratory [5–8]. The naphthenic acid molecule has a carboxylic polar group, and at the other end of the hydrocarbon chain it contains a pentatomic ring with side hydrocarbon groups of different lengths. Naphthenic acid is also known as a W/O microemulsion-forming reagent, but the pentatomic ring is too large to form a proper curvature to meet the requirement of forming microemulsion droplets.

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Octanol has been proved to be a proper cosurfactant to decrease the curvature of adsorbed films of naphthenic acid. Such that mixed solvent of 1-octanol and *n*-heptane is used in this study. In addition, as true for other acid extractants, only the salt form of the naphthenic acid ("saponified" naphthenic acid or naphthenate) can form W/O microemulsion in organic diluents.

A special amino acid, DL-2-amino-4-sulfonobutyric acid (DLH), is an important free amino acid in the central nervous system of human body [13,14], with a characteristic chemical structure in its sulfonate group at the opposite end from the amino and carboxylate groups of the molecule. Contrary to the hydrophobic nature of amino acids, the DLH molecule is rather hydrophilic, with high hydration affinity and solubility in water, because of the three polar groups on a tetratomic hydrocarbon chain. In its crystal lattice, one DLH molecule can form 10 H-bonds with its neighbors [15]. From the point of view of the conventional extraction process [9,10], complex formation between the extractant and metal ions and its hydration affinity depend on the structure of the surfactant molecule, in particular its polar head groups. Generally, the amino acid residues are thought to be hydrophobic and act as a cosurfactant in reversed micelle systems [16]. In the case of DLH, we have found that the carboxyl and sulfonate groups can coordinate with Na^+, K^+, and Ca^{2+} ions to form complexes characterized by FTIR and FT-Raman spectroscopic analysis [17]. In addition, FTIR and FT-Raman spectroscopic results have proved that the H-bond skeleton of DLH in the solid state was rearranged in D_2O solution [14], yielding a different hydration network with heavy water molecules. The effect of introducing an amino acid containing NH_3^+, COOH, and SO_3^- groups into the microemulsion system on the microstructures of the various species is a matter of peculiar interest. In this study, FTIR and PCS (photon correlation spectroscopy) techniques were employed for detecting the structural changes of various species contained in W/O microemulsion system.

2. Experimental section

2.1. Materials and preparation of samples

Naphthenic acid was a product of Fluka Chemika and redistilled under reduced pressure. The molecular weight of the distillate was determined to be 227. The purified naphthenic acid was diluted with *n*-heptane and refluxed with potassium metal for about 6 h. The product was found 80% saponified and then adjusted to 1.16 M (0.23 M naphthenic acid (HR) + 0.93 M K-naphthenate (KR)) as a stock solution by adding 1-octanol and *n*-heptane. The volume ratio of the 1-octanol to *n*-heptane in the stock solution was 1/3. The aggregate system was expressed as 0.23 M HR + 0.93 M KR (surfactant)/mixed solvent. Various amounts of water were added to a fixed volume of the stock solution to obtain a series of samples of the aggregation systems (S-I). In order to study the effect of DL-homocysteic acid (DLH) on the aggregate system, various amounts of aqueous solution of 0.1 M DLH were added to a fixed volume of the stock solution to obtain the second series of samples (S-II).

2.2. Solubilization capacity measurement

Various amounts of 0.1 M DLH solutions were added to different portions of a fixed volume of stock solution at room temperature, and then additional water was added until the clear solution became turbid indicating that the saturation was reached. The total amount of water added to the sample was expressed as molar ratio of water to surfactant at saturation by W_0^s to distinguish from W_0 below saturation. The effect of DLH on the solubilization capacity was then represented by plotting A_0 (the molar ratio of DLH to surfactant) versus W_0^s, as shown in Fig. 1.

2.3. FTIR and PCS (photon correlation spectroscopy) measurement [6,7]

FTIR spectra of all samples were recorded in the range of 900–4000 cm^{-1} with a Nicolet Magna IR 750 II spectrometer using a BaF_2 window [9]. Each sample was recorded with 32 scans at a spectral resolution of 4 cm^{-1}. PCS measurements were carried out with a self-constructed goniometer with a Spectra-Physics 2017 argon ion laser at a wavelength of 514.5 nm. The results are expressed as particle size distribution histograms shown in Fig. 2.

3. Results and discussion

3.1. Effect of DLH on solubilization capacity of water in W/O microemulsion

Fig. 1 is the plot of A_0 (molar ratio of DLH to surfactant) versus W_0^s (molar ratio of water to surfactant at saturation)

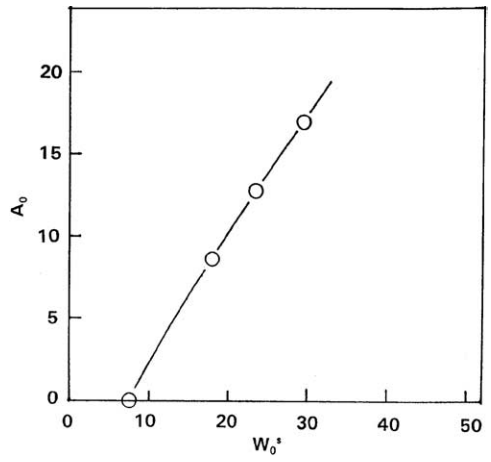

Fig. 1. Saturation water content (W_0^s) as a function of DLH content ($A_0 \times 10^{-3}$) in aggregation systems of 0.23 M HR + 0.93 M KR/mixed solvent (25% 1-octanol + 75% *n*-heptane).