The interaction between polymer and surfactant as revealed by interfacial tension

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Abstract: The aging of aqueous ethyl(hydroxyethyl)cellulose (EHEC) solution and mixed solutions of polymer and sodium dodecyl sulfate (SDS) in contact with cyclohexane was studied by measurement of interfacial tension, using the pendant drop method. Studies were performed over the concentration ranges 0–18 mM SDS with fixed concentration 0.2% w/w EHEC, and 0–16 mM SDS with no polymer added. EHEC was found to be very surface active, and the kinetics of polymer adsorption to the water/cyclohexane interface is extremely slow. The mixed solutions of polymer and surfactant showed a more typical timescale for adsorption. The variation in the equilibrium interfacial tension of the mixed polymer-surfactant solutions was assumed to reflect the variation of the activity of polymer, and the interactions between the polymer and other particles in the system. The observed effects were explained as due to the changes in polymer-solvent and polymer-surfactant interactions, resulting in a changed conformation of the polymer, as well as the formation of micelle-like clusters and free micelles.

Key words: Interfacial tension; cellulose derivative; surfactant; micelle; polymer-surfactant interaction; pendant drop method

Introduction

Polymers are used widely in pharmaceutical systems as adjuvants, suspending and emulsifying agents, flocculating agents, adhesives, packing and coating materials, and increasingly, as the basis of drug-delivery systems [1]. Development of polymer applications requires good characterization of polymer properties and knowledge on how and why polymers interact with other substances, e.g., surfactants. Drastic changes in general properties of aqueous polymer-surfactant solutions is observed and this has given rise to a large number of studies using different methods [2, 3]. Novel studies of aqueous solutions of sodium dodecyl sulfate (SDS) and ethyl(hydroxyethyl)cellulose (EHEC) have indicated very interesting possibilities to investigate detailed features of the interaction polymer-surfactant [4–6]. The present investigation, dealing with the surface activity of aqueous EHEC-SDS solutions at the water/cyclohexane interface, was started as a supplementary examination. Today, knowledge on the surface activity of polymers and polymer-surfactant solutions is limited. The surface tension of aqueous solutions for a number of moderately surface-active polymers have been measured by common methods (capillary rise method, ring tensiometry, drop weight method). In no case did these aqueous polymer solutions display a constant steady-state surface tension, probably due to the high viscosity of polymer solutions, the slow molecular diffusion, and the possible change of the polymer conformation. In the present study, the pendant drop method is used since it enables surface and interfacial tension measurements to be made over a long time scale without disturbing the liquid/liquid interface. The cyclohexane/water system was used for experimental reasons. Compared to the air/water system, an increased phase stability, suitable drop shape and size, and a reduced inconvenient wetting on the outside of syringe capillary are obtained.
Nahringbauer, Interaction between polymer and surfactant

Experimental

Materials

EHEC is a cellulose ether manufactured by the partial substitution of cellulose with ethyl groups and oligo (ethylene oxide) chains. The polymer studied is a special grade of EHEC (CST-103), molecular weight 200000 as determined by light scattering. The molar ratio of ethyl to ethylene oxide groups is high which makes it relatively hydrophobic. On the average 1.5 hydroxyl groups per polymer segment are substituted by ethyl giving rise to ether groups, and on the average 0.7 oxyethylene groups per segment form oligo(ethylene oxide) chains. The cloud point of 0.2% w/w aqueous polymer solution is approximately 27°C. Furthermore, the samples are manufactured by a heterogeneous reaction in which the substituents are not evenly distributed along the cellulose backbone. This means there might be regions which are hydrophobic in nature and regions which are hydrophilic. The stock solution of EHEC was prepared according to a standard technique [7], and carefully dialyzed and filtered to get a salt-free and homogeneous solution. SDS 99.9% pure was used as supplied. The stock solution of SDS was prepared by dissolving SDS in doubly distilled and filtered water to a concentration of 0.1 M. The solutions for interfacial tension studies were prepared by weighing the required amounts of the EHEC stock solution into appropriately diluted SDS stock solutions. The order of adding the components was observed to be important as it greatly affects the properties of the solutions. After mixing, significant changes in solution viscosity was observed over extended times. Cyclohexane, 99.95% pure aristar, was used as supplied. The densities were determined in a digital densitometer with an accuracy exceeding 0.0015 kg/m³.

Apparatus and method

The method of measurement is based on the pendant drop technique. The apparatus used is described elsewhere [8]. Essentially, an image of the drop is projected onto photographic technical film by a beam of parallel laser light. The range of drop volume is 1–3 mm³. The coordinates of the drop contour, magnified about 200 times, are measured to within ±1 μm directly from the film by means of a profile projector on line with an Apple Macintosh computer.

Theoretical curves, obtained by numerical integration of the Young-Laplace equation are then fitted to the data (around 100 points). The aging of the aqueous solution in contact with cyclohexane is recorded by a set of exposures. The image of the same drop of aqueous solution, pendant in cyclohexane, is exposed on a film 20–40 times, and the images provide the registration of interfacial tension at increasing drop age (5 s to several hours). The time of exposure is 1/250 s. The present studies were performed in a climate room at the temperature of 19.5 ± 0.5°C.

Results and discussion

Surface activity of EHEC at the water/cyclohexane interface

The heterogeneous substitution of hydrophilic ethylene oxide groups and hydrophobic ethyl groups along the cellulose backbone has made EHEC very surface active. Furthermore, the kinetics of polymer adsorption to the water/cyclohexane interface is extremely slow.

As shown in Fig. 1, initially the interfacial tension for the aqueous solution containing 0.2% w/w EHEC decreases sharply, and then it levels off slowly to 3.5 mN/m, which is one-third of its initial value. Since the equilibrium value was not achieved

![Fig. 1. Interfacial tension γ(t) for cyclohexane/aqueous EHEC solution as a function of adsorption time](image-url)