Abstract  Scattering studies have been performed on a mixed micellar system containing a cationic surfactant C16TAB (hexadecyl trimethylammonium bromide) and a non-ionic surfactant C12E6 (hexaethylene glycol monododecyl ether). Light-scattering measurements indicate that the addition of salt (KBr) initiates unidirectional growth of the mixed micelles into elongated aggregates. These elongated micelles exhibit some flexibility and can be characterised by scaling laws used to model polymer solutions. Small-angle neutron scattering (SANS) measurements indicate that the micelles usually prefer to exist as a single population of homogeneous aggregates, although evidence is obtained to suggest that some degree of de-mixing may occur in more dilute surfactant solutions containing salt.

Key words  Mixed micelles – light scattering – small-angle neutron scattering – growth effects – micelle composition

Introduction

Micelles of cationic surfactants often undergo a transition from spheres to rods in the presence of salt and form flexible worm-like chains [1–4]. This process of unidirectional growth has been attributed to screening of the charged head-groups by the salt ions which favours packing of the surfactant molecules into rod-like micelles [5]. In this paper we examine salt-induced micelle growth from an aqueous mixed surfactant system containing the cationic surfactant C16TAB (hexadecyl trimethylammonium bromide) and the non-ionic surfactant C12E6 (hexaethylene glycol monododecyl ether) at C16TAB mole fraction of 0.55. A combination of light and small-angle neutron scattering has been used to obtain information on overall dimensions and shape of the micelles. In addition, the contrast variation method has been used to determine the composition of the micelles.

Light scattering measurements

Static light scattering

The excess scattered intensity from a dilute dispersion of weakly interacting micelles may be approximated by:

\[ K(c - c_0) / \Delta R_0 = [1 + \langle R_g^2 \rangle_2 q^2/3]/M + 2 B_2 (c - c_0), \]

where \( c \) is the total surfactant concentration, \( c_0 \) is the critical micelle concentration, \( K \) is a constant, \( M \) is the weight-average micelle mass, \( B_2 \) is the second virial coefficient and \( q \) is the scattering wave vector; \( q = 4\pi n_0 / \lambda_0 \sin(\theta/2) \), where \( \theta \) is the scattering angle and \( \lambda_0/n_0 \) is the wavelength of incident light in the sample. The parameter \( \Delta R_0 \) is the Rayleigh ratio of the micelles which is obtained from the difference between the Rayleigh ratios of the surfactant solution and the solvent medium. \( R_g \) is the radius of gyration.

Scattering studies of mixed micelles formed from C16TAB and C12E6 surfactants

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Dynamic light scattering

In dynamic light scattering experiments the apparent diffusion coefficient \(D_q\) is related to the decay rate of the time correlation function \(G\) by:

\[
D_q = \Gamma / q^2 . \tag{2}
\]

The apparent diffusion coefficient may contain contributions from both rotational and translational motion. In order to obtain the pure translational diffusion coefficient \(D_o\) it is necessary to extrapolate the apparent diffusion coefficient to zero scattering wave vector. The hydrodynamic radius \(R_h\) of the micelles may then be calculated from the translational diffusion coefficient according to the Stokes–Einstein equation.

\[
R_h = kT/6\pi \eta D_o , \tag{3}
\]

where \(\eta\) is the solvent viscosity, \(k\) is the Boltzmann constant and \(T\) is the absolute temperature.

Results

For solutions containing KBr the reciprocal scattering intensity (expressed as \(K/(c - c_0)/AR_o\)) is first seen to decrease as a function of surfactant concentration before passing through a minimum and then slowly increasing again. This behaviour is reflected by the increase and then decrease in \(R_g\) indicated in Fig. 1. The initial decrease in reciprocal scattering intensity can be attributed to a process of micelle growth provided that interactions between the micelles are negligible (i.e. \(B_2 \sim 0\)). This assumption is considered to be reasonable given that KBr is expected to screen out electrostatic repulsions from dissociated C\(_{16}\)TAB molecules. The mass of the micelles \(M\) can then be estimated from the minimum in reciprocal scattering intensity. Using this approach micelle masses are found to be \(2.3 \times 10^5\) in 0.1 M KBr and \(1.3 \times 10^6\) in 0.5 M KBr. These values compare with a lower micelle mass of \(\sim 7 \times 10^4\) measured from SANS for the mixed micelles in pure water.

The concentration where the minimum in reciprocal scattering intensity occurs may be identified as a “cross-over” concentration, \(c^*\), between a dilute and semi-dilute regime. This treatment, originally developed for semiflexible polymers, has also been used to describe cationic micelles which undergo similar growth processes in the presence of salt to form worm-like chains. Below \(c^*\), in the dilute region, the micelles are viewed as diffusing almost independently of each other, whereas on passing into the semi-dilute region micelle growth has proceeded to an extent that the micelles start to overlap and form an entangled network. In the semi-dilute region the scattering is now dominated by correlation lengths \(\xi\) which characterise the entangled network and not by the size of individual micelles. This idea of micelle growth is supported by dynamic light scattering results. The translational diffusion coefficient \(D_o\) is found to pass through a minimum at roughly the same concentration as the maximum in \(R_g\) (Fig. 1).

Scaling behaviour can provide useful information on the conformation and flexibility of micelles. The scaling relationship between micelle mass and radius of gyration is sensitive to micelle shape [6]:

\[
R_g \sim M^n . \tag{4}
\]

Figure 2 shows a double logarithmic plot of \(R_g\) versus micelle mass for micellar solutions in 0.5 M KBr. The exponent of 0.53 derived from this plot is characteristic of a random coil structure. Rigid, thin rods are expected to give an exponent close to unity.