

Article

Relationship between Some Colloidal Properties of Non-Ionic-Anionic Surfactant Mixtures

Roland Nagy, Réka Kothencz, Máté Hartyányi *  and László Bartha

Department of MOL Hydrocarbon and Coal Processing, University of Pannonia, H-8200 Veszprém, Hungary; nroland@almos.uni-pannon.hu (R.N.); rekakothencz@gmail.com (R.K.); bartha@almos.uni-pannon.hu (L.B.)

* Correspondence: hartyanyi.mate@mk.uni-pannon.hu

Abstract: Non-ionic surfactants are compatible with different types of materials, therefore they can be applied in various packages. Fatty-acid derivatives as non-ionic surfactants and their mixtures were investigated to study their colloidal behavior. The HLB value, the particle size, the emulsification capacity and the interfacial tension of various commercial, non-ionic surfactants, and their mixtures with sodium lauryl-ether-sulfate (SLES), were determined. The surfactant mixtures were prepared in different non-ionic: anionic surfactant ratios to examine their effect on several surfactant characteristics. The interfacial tension between the oil phase and aqueous phase was measured using the spinning drop method and the average hydrodynamic diameter of surfactants in the aqueous solution was determined using the dynamic light scattering method. The relationship between various colloidal properties of surfactants was investigated. It was found that there is a significant relationship between the colloidal characteristics and the structure of surfactants that can contribute to their efficient selection method.

Keywords: surfactants; HLB value; particle size; emulsification capacity; interfacial tension



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1. Introduction

A large fraction of surfactants is concerned with cleaning operations; however, the demands of other technological areas have also added greatly to the enhanced role of surfactants. The applications of surfactants in pharmaceuticals, petroleum recovery processes, high-tech applications and other medicine are placing more demands on our ability to understand and manipulate interfaces through the action of surface-active agents [1,2]. According to emulsification principles, a combination of a high and low HLB emulsifier is often more effective than the use of a single emulsifier. The optimal combination of ionic and non-ionic surfactants and their synergism can be essential in terms of the application area [3].

Petroleum-related occurrences of emulsions and foams are widespread and important to industrial productivity [4]. Both emulsions and foams may be applied at all stages in the petroleum recovery and processing industry, and both have important properties that may be desirable in some process contexts and undesirable in others [5,6]. The widespread interest in microemulsions and their use in industrial applications is based mainly on their high solubilization capacity for both hydrophilic and lipophilic compounds, and their large interfacial areas and ultra-low interfacial tensions achieved when they coexist with excess aqueous and oil phase [4,7].

Span and Tween surfactants are found in a diverse range of household consumer products and are useful as emulsifiers, solubilizers, wetting agents and dispersants [8]. Sodium lauryl-ether-sulfate (SLES) is an anionic detergent and surfactant found in many personal care products (soaps, shampoos, toothpaste, etc.) as a very effective foaming agent. By using combinations of Spans and Tweens with SLES it is possible to prepare a variety of excellent emulsifying systems.

Our aim was to investigate the relationship between the surfactants' structural properties and some colloidal properties. The HLB of the mixtures of surfactants was calculated and the IFT was measured using a spinning drop tensiometer. The particulate size distribution of surfactants has been studied using dynamic light scattering measurements. The micelle shape was determined according to Tanford's method. Knowledge of the above properties and their relationship allows the efficient application of surfactants and surfactant mixtures.

2. Materials and Methods

The mixture of anionic surfactant sodium lauryl-ether-sulfate (SLES) with commercial non-ionic surfactants marketed under Span and Tween product names were used in this work. The Span products were sorbitan esters, and the Tweens were ethoxylated Spans.

The chemical type of Span and Tween products and some other commercial surfactants are shown in Table 1.

Table 1. The chemical identity of Span and Tween products.

Product Name	Chemical Identity	Producer	CAS Number
Span 20	Sorbitan monolaurate	Sigma-Aldrich	1338-39-2
Span 40	Sorbitan monopalmitate	Sigma-Aldrich	26266-57-9
Span 60	Sorbitan monostearate	Sigma-Aldrich	1338-41-6
Span 80	Sorbitan monooleate	Sigma-Aldrich	1338-43-8
Tween 20	PEG-20 sorbitan monolaurate	Sigma-Aldrich	9005-64-5
Tween 40	PEG-20 sorbitan monopalmitate	Sigma-Aldrich	9005-66-7
Tween 60	PEG-20 sorbitan monostearate	Sigma-Aldrich	9005-67-8
Tween 80	PEG-20 sorbitan monooleate	Sigma-Aldrich	9005-65-5
Tween 85	PEG-20 sorbitan trioleate	Sigma-Aldrich	9005-70-3
Triton X-100	Octyl phenol ethoxylate	Sigma-Aldrich	9002-93-1
Lutensol XP 30	Alkyl polyethylene glycol ether	BASF	160875-66-1
APG-70 (0810)	Alkyl polyglycoside	BASF	68515-73-1

The surfactant mixtures contained non-ionic and anionic surfactants in a 50:50 mass ratio (based on previous experience) and were dissolved in distilled water at 1 w/w% total concentration. The composition of surfactant mixtures is shown in Table 2.

Table 2. Components of surfactant mixtures.

Mark of the Surfactant Mixture	Non-Ionic Surfactant	Anionic Surfactant
M-1	Span 20	SLES
M-2	Span 40	SLES
M-3	Span 60	SLES
M-4	Span 80	SLES
M-5	Tween 20	SLES
M-6	Tween 40	SLES
M-7	Tween 60	SLES
M-8	Tween 80	SLES
M-9	Tween 85	SLES
M-10	Triton X	SLES
M-11	Lutensol XP 30	SLES
M-12	APG	SLES

For the measurements of interfacial tension and emulsifying capacity, a model crude oil was prepared. 60 cm³ of n-heptane was mixed with 40 cm³ of toluene in a conical flask. Before mixing, 0.1 g of asphaltene was dissolved in the toluene. The recipes of model crude oil are based on the study of Alimi and Oyediji [9].

2.1. Interfacial Tension (IFT)

The interfacial tension between the aqueous phase of the surfactant mixture (in distilled water 1 *w/w*% concentration) and the model oil was measured using the spinning drop method. The measurement was carried out in a Krüss SDT tensiometer. While the rotation of the cylinder exerts a centrifugal force on its wall, the drops of the lower density fluid are deformed in an elongated form. The interfacial tension between the two fluids can be calculated from the form of the drops using the Young–Laplace-fit method.

2.2. Particle Size Analysis

The particle size (micelles size) and distribution of the samples were measured using dynamic light scattering using a Malvern Zetasizer Nano ZS instrument. The hydrodynamic radius was determined by dynamic light scattering and estimated from the particles' diffusivity using the Stokes–Einstein equation. The apparatus uses a 5 mW HeNe laser at a wavelength of 633 nm at a 90° scattering angle. Independent triplicates of each sample over 5 runs were measured in a PCS8501 square glass cuvette. The average peak values of particle diameter (nm) for the different samples were calculated.

2.3. Emulsifying Capacity (EC)

10 cm³ of model crude oil and 10 cm³ aqueous solution of surfactant mixture solution (containing 15 g/L surfactant mixture) were measured in a cylinder. The liquid mixture was shaken at room temperature for 7 complete translation cycles and the quantity of different phases was measured 30 min after. Then the samples were shaken again and placed in an oven at 80 °C and after 1 h the volumes of the phases were read again. The quantities of the aqueous phase and emulsion phase are given as percentages of the total liquid volume.

2.4. Solubility in Water (Transmittance)

The surfactant mixture was dissolved in distilled water at 1 wt% concentration and the turbidity was then measured using a spectrophotometer. The solubility in water is characterized by the transmittance value (0% completely cloudy, 100% transparent).

2.5. Shape of Micelles

To determine the shape of the formed micelles (mixed micelles), some parameters were used that could give the most likely shape of micelles. The length (1) and the volume (2) of the hydrocarbon tail can be empirically determined by the method of Tanford [10]:

$$l = (0.154 + 0.1265n_c) n \quad (1)$$

$$v = (27.4 + 26.9n_c) \times 10^{-3} \text{ nm}^3 \quad (2)$$

where n_c = number of carbon atoms in the saturated hydrocarbon chain.

Based on the average molar ratio, the volume (v) and the length (R) of the surfactant tail can be given Equations (3) and (4) [11–13]:

$$R = \sum_{i=1}^N x_i l_i \quad (3)$$

$$v' = \sum_{i=1}^N x_i v_i \quad (4)$$

where:

x_i = mole fraction of component “i” in the mixed micelle.

l_i = length of the hydrocarbon chain of the respective surfactant molecule.

v_i = volume of the tail of a molecule of the *i*th component.

By introducing the parameter a_0 , the surface of the head group per molecule of the surfactant at the micelle–solution interface and the thermodynamic interaction between them are involved, thus the packing parameter (P) can be calculated (5) [10,11]:

$$P = \frac{v'}{a_0 R} \quad (5)$$

where a_0 = equilibrium area per molecule at the aggregate interface.

Only the headgroup controls the equilibrium aggregate structure via the headgroup area, the tail does not have any influence on the shape and size of the aggregate. A bigger head group has a larger value of a_0 and the formation of spherical micelles is more probable. Table 3 shows the relationship between the packing parameter and the geometrical forms of micelles.

Table 3. Geometrical relations for spherical, cylindrical, and bilayer aggregates.

$P < 1/3$	Spherical or ellipsoidal micelles
$1/3 < P < 1/2$	Large cylindrical or rod-shaped micelles
$1/2 < P < 1$	Vesicles and flexible bilayers structure
$P = 1$	Planar extended bilayers
$P > 1$	Reversed or inverted micelles

3. Results

3.1. Determination of the Shape of Micelles

The calculated values of P parameters of each used surfactant mixtures are shown in Table 4.

Table 4. Value of P parameter of each surfactant mixture.

Mark of the Surfactant Mixture	Value of P Parameter
M-1	0.210
M-2	0.210
M-3	0.210
M-4	0.210
M-5	0.211
M-6	0.212
M-7	0.212
M-8	0.212
M-9	0.212
M-10	0.191
M-11	0.187
M-12	0.201

According to the determination of the shape of micelles by Tanford et al. [10], spherical or ellipsoidal micelles are probably formed in the surfactant mixtures, which assumes an equilibrium micelle structure based on the free energy model. Since the micelles of the surfactant mixtures are of the same shape, they can be compared.

3.2. Determination of HLB Values

HLB values of an additive, that is, the HLB of the mixture of surfactants, consisting of fraction x of A and $(1 - x)$ of B is assumed to be the algebraic mean of the two HLB numbers [3], i.e.,

$$HLB_{\text{mixture}} = x HLB_A + (1 - x) HLB_B \quad (6)$$

HLB values of surfactant mixtures were calculated using the equation above (6). Spans have low HLB values ranging from 4.3 to 8.6, while Tweens, as they are polyoxyethylene derivatives of Spans, are more hydrophilic and have higher HLB values ranging from

11.0 to 16.7. As SLES have relatively high HLB (40), their mixtures with Spans and Tweens vary in a narrow range between 22–29.

3.3. Surfactant Mixtures of Non-Ionic Surfactants with the Same Structure in Water Soluble Range (HLB 22–29)

The hydrodynamic diameters of the surfactant mixture solutions containing non-ionic surfactants with the same structure were determined (PDI = 0.7–0.8) and the results were represented as the function of transmittance (Figure 1).

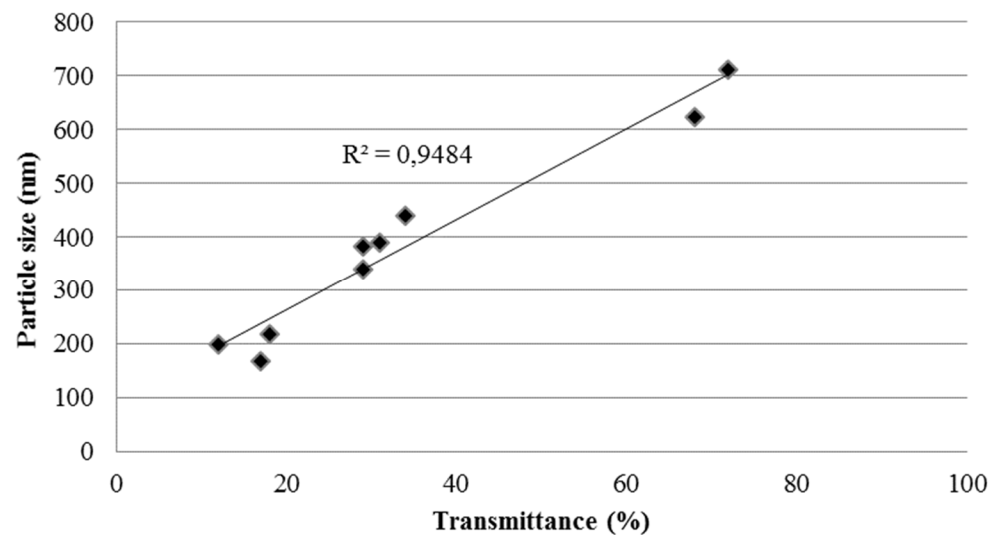


Figure 1. Average particle size vs. transmittance for surfactant mixtures from non-ionic surfactants with the same structures.

It was found that the increase in the average particle size of the micelles in the aqueous solution of surfactants has resulted in an increase in transmittance which can be explained by a new formation of micelles.

The relationship between the emulsification capacity and IFT of surfactant mixture solutions from non-ionic surfactants with the same structure is shown in Figure 2.

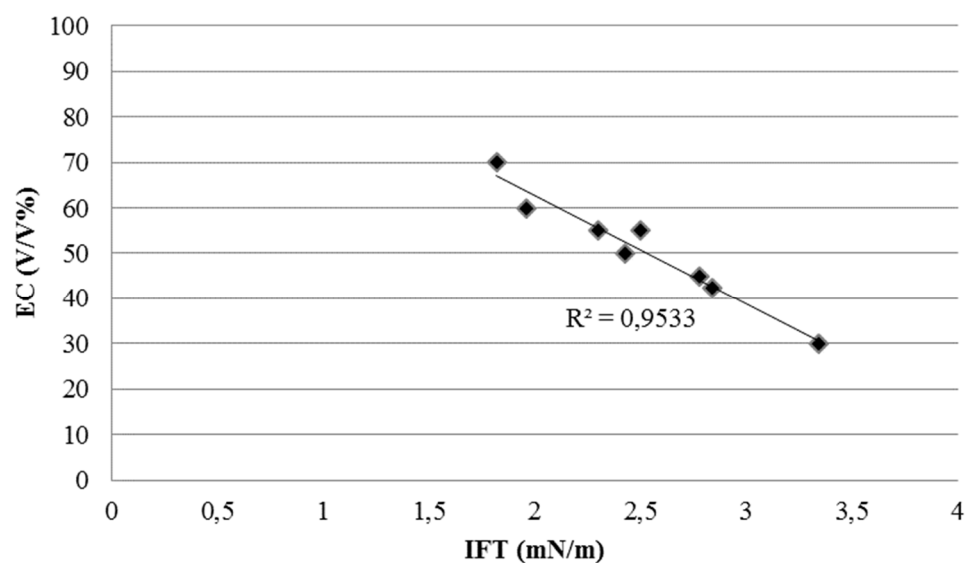


Figure 2. Emulsification capacity vs. IFT for surfactant mixtures from non-ionic surfactants with the same structures.

The increasing interfacial tension reduces emulsifying ability, thus there is a significant relationship between the interfacial tension and the emulsification capacity.

3.4. Surfactant Mixtures of Non-Ionic Surfactants with Different Structures in Water Soluble Range (HLB 22–29)

The relationship between the average particle size (PDI = 0.7–0.9) and the transmittance of surfactant mixtures from non-ionic surfactants with different structures (M-1, M-5, M-8, M-10, M-11 and M-12) were examined (Figure 3).

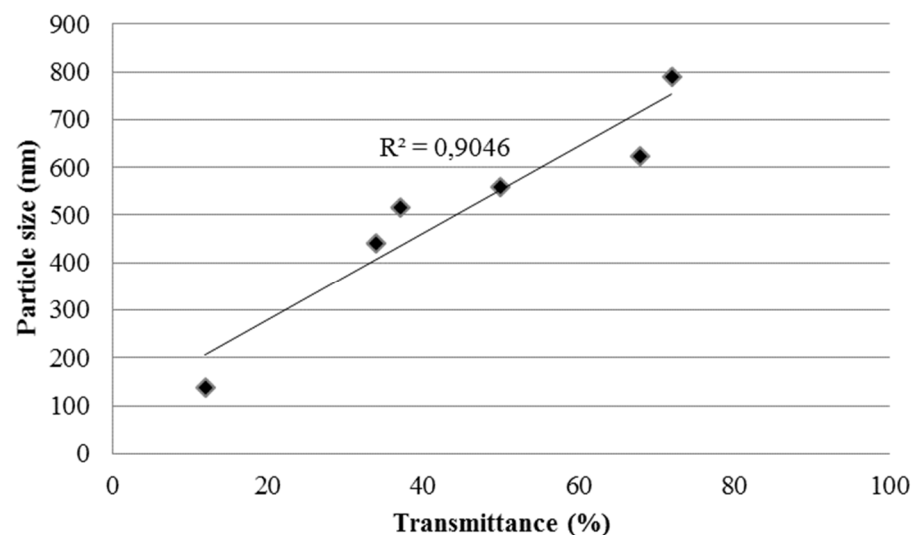


Figure 3. Average particle size vs. transmittance for surfactant mixtures from non-ionic surfactants with different structures.

It was observed that the relationship between the hydrodynamic diameter and the transmittance of the surfactant mixtures from non-ionic surfactants with different structures was nearly the same as for the surfactant mixtures from non-ionic surfactants with the same structure. The transmittance increases with the growing average particle size, thus the formation of micelles can be assumed in this case as well (Figure 4).

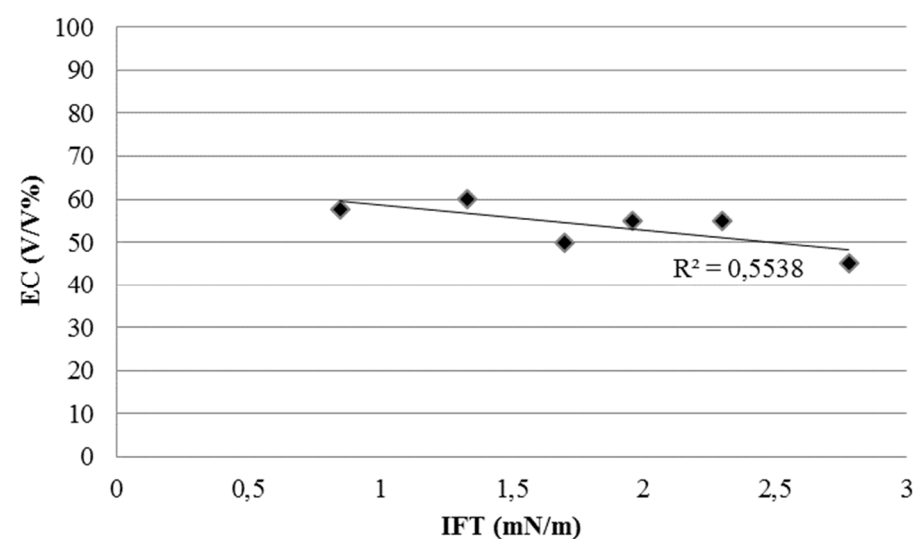


Figure 4. Emulsification capacity vs. IFT for surfactant mixtures from non-ionic surfactants with different structures.

Contrary to Figure 2, only a slight relationship can be observed between the emulsification capacity and the IFT of surfactant mixture solutions from non-ionic surfactants with different structures. However, the tendency is also the same in this case.

The aqueous solutions of the tested surfactant mixtures have been found to be effective in every case, therefore they can be used in a relatively wide range of applications.

4. Discussion

In summary, we can conclude that there is a significant linear relationship between the particle size and the transmittance of the aqueous solutions of surfactant mixtures containing non-ionic surfactants of the same structure and also with different structures. Higher interfacial tension reduces the emulsifying capacity of the surfactant mixtures with the same and different structures, however the relationship between interfacial tension and emulsifying capacity can be determined only in the case of surfactant mixtures of non-ionic surfactants with the same structure. Based on the determination of the shape of the micelles by Tanford [10], it can be assumed that spherical or ellipsoidal micelles are formed in the surfactant mixture solutions studied in this work.

5. Conclusions

The presented method is also suitable for the selection of commercial surfactants. The analysis of the relationship between the various properties allows the estimation of the applicability of commercial surfactants in different fields of practical use. The mix ratio of the anionic surfactants, which are used to produce a surfactant mixture with the target HLB-value, can be calculated without laboratory measurements using the revealed linear correlations. The predictability of surfactants in EOR processes can be increased according to colloid chemical measurements. The micelle shape and colloid properties relationships were investigated. The results of the investigated series of surfactant/surfactant mixtures, which are also important from an environmental point of view, contribute to their efficient application.

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