

CHARGE DES ÉMULSIONS DE GOUTTELETTES COUVERTS DE SURFACTANTS NON IONIQUES

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CHARGE OF EMULSION DROPLETS COVERED WITH NONIONIC SURFACTANTS

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RÉSUMÉ

On a mesuré la mobilité électrophorétique des gouttelettes d'huile en présence des surfactants non-ioniques (Tween 20, Span 20 et $C_{16}EO_8$ ultra-pure). On a obtenu pour le ζ -potential des valeurs considérablement négatives. On a fait des expériences avec de gouttelettes d'huile pure pour comprendre mieux le mécanisme des interfaces de se charger. On a utilisé quatre différents types d'huile. On a fait attention pour ne pas admettre des artefacts, dus à la présence des surfactants ioniques.

Les résultats ont indiqué que les gouttelettes d'huile pure sont négativement chargées et l'amplitude de leur ζ -potential est fort indépendante du type d'huile utilisé. Les résultats des différentes expériences ont montré que les charges négatives représentent des ions d'hydroxyles adsorbés, dus à la dissociation de l'eau. On a évalué l'énergie spécifique de l'adsorption - 25 kT pour un ion hydroxyle. L'amplitude de cette énergie suggère que l'adsorption est liée à un processus de formation de liaison à hydrogène entre les ions hydroxyles et les molécules d'eau situées à la surface, et qui est énergétiquement favorable.

Les mesures en présence de surfactants non-ioniques ont montré que l'amplitude du ζ -potential diminue avec l'augmentation de la concentration des surfactants. Ce fait prouve que les surfactants non-ioniques changent le potentiel électrostatique et ne le causent pas, comme on a pensé auparavant. Sans aucun doute, les interactions électrostatiques jouent un rôle important pour les propriétés des émulsions, stabilisées par des surfactants non-ioniques et en présence de peu de sel.

ABSTRACT

The electrophoretic mobility of oil droplets in the presence of the nonionic surfactants Tween 20, Span 20 and ultra-pure $C_{16}EO_8$ was measured. Significant negative values of the ζ -potential were obtained. Experiments with pure oil droplets were performed to clarify the mechanism of the interfacial charging. Four different oils were used. Special precautions were undertaken to avoid artefacts caused by the presence of ionic surfactant impurities.

The results show that the pure oil droplets are negatively charged and the magnitude of their ζ -potential strongly depends on pH and the ionic strength of the aqueous phase. The electrophoretic mobility is almost independent on the specific non-polar oil. The results from different experiments lead to the conclusion that the negative charges originate from the adsorption of OH^- , released by the dissociation-association equilibrium of the water molecules. The specific adsorption energy is estimated to be 25 kT per ion. The magnitude of this energy suggests that the adsorption is connected to an energetically favored process of hydrogen bonding between the hydroxyl ions and the water molecules at the interface.

The measurements in the presence of nonionic surfactants demonstrated a decrease in the magnitude of the ζ -potential upon increase of the surfactant concentration. This implies that the nonionic surfactants modify the electrostatic potential at the oil-water interface, rather than to create it, as previously thought. There is no doubt that the electrostatic interactions play a substantial role in the properties of emulsions stabilised by nonionic surfactants at low ionic strength.

1. Introduction

The properties and stability of dispersions are greatly influenced by the presence of ionic charges on the particle surfaces [1-6]. In several studies spontaneous charging of oil-water interfaces was detected in the presence of *nonionic* surfactants whose molecules are not ionizable [7,8]. This fact was explained with possible specific adsorption of hydroxyl ions at the interface due to hydrogen bonding with the polyoxyethylene chains of the surfactant molecules [8]. This hypothesis was used to explain the strong dependence of the measured electrical potentials on the acidity of the aqueous phase.

Even earlier it was found out [9-11] that the interface between water and non-polar oil could possess substantial negative charge even in the absence of any surfactant. In spite of the experimental evidences that the oil-water interface is negatively charged, and of the importance of this phenomenon for emulsion behaviour and stability, the origin of the charge is by no means well understood [12].

In order to reveal the origin of the charges at the pure oil-water interface and in the presence of nonionic surfactants, we carried out a systematic study of the role of different factors (surfactant concentration, oil type, acidity and ionic strength of the aqueous phase, etc.) on the electrophoretic mobility (EPM) of oil droplets dispersed in aqueous medium.

2. Materials and Methods

2.1. Materials. The nonionic surfactants hexadecyl polyoxyethylene-8, $C_{16}(OE)_8$ (ultra-pure brand, Nikkol, Japan), polyoxyethylene-20 sorbitan monolaurate (Tween 20), and sorbitan monolaurate (Span 20), were used. Tween 20 and Span 20 were products of ICI, Great Britain. The water for the experiments was obtained from Milli-Q Organex system (Millipore). Four different non-polar organic liquids were used as oil phases: xylene (*p.a.* grade), dodecane (Sigma), hexadecane (Sigma) and perfluoromethyldecalin (Rhône-Poulenc S. A., commercial name Flutec PC-7). The xylene, hexadecane and perfluoromethyldecalin were purified by passing through a glass column filled with adsorbent for polar contaminations (Florisil) [13]. Dodecane was used as received. The sodium chloride (Merck product) was heated at 500°C for 6 hours to remove organic impurities. The sodium hydroxide and the hydrochloric acid, used for adjustment of pH of the aqueous solutions, were *p.a.* products and were used without further purification.

All vessels and glassware were cleaned by immersion into chromic acid for at least 24 hours and consecutive abundant rinsing with purified water.

2.2. Methods for emulsion preparation. The water soluble surfactants were initially dissolved into the aqueous phase, while the oil soluble Span 20 was initially dissolved in the oil. The water and oil phases were put in contact for pre-equilibration at least 24 hours before preparing the emulsion. Emulsions containing nonionic surfactants were prepared by mixing the pre-equilibrated phases with a rotating blade laboratory homogenizer at approximately 3000 rpm. Some of the emulsions without surfactant were also prepared in the same way. The mean droplet diameter in these emulsions was several micrometers.

In order to ensure highest purity of the systems without surfactants, we developed another method for preparation of xylene-in-water emulsions without using any mechanical agitator [18]. The xylene and water were brought into contact and the mixture was heated in a thermostat at 60°C for one hour. Due to the increased solubility of xylene in water at higher temperatures, a small part of the xylene dissolved in the aqueous phase. When the system was afterwards cooled down to 22°C (the temperature at which the measurements were performed) the excess of the dissolved xylene separated as fine emulsion droplets. The measurements of the droplet size showed that the obtained emulsions had initial droplet diameter of 100-200 nm. The mean size of the droplets slowly increased and reached micrometer values after 5 to 10 minutes. The electrophoretic measurements with the surfactant-free emulsions prepared in this way were much

more reproducible than the measurements with emulsions obtained by the homogenizer. This new method allowed preparation of samples of higher purity that did not come in contact with a homogenizer and were kept in closed all-glass environment.

2.3. Electrophoretic mobility and droplet size measurements. Most of the measurements were carried out on a *Zetasizer IIC* equipment (Malvern Instruments, Ltd.). For comparison, several experiments were repeated by using Zeta-Meter system 3.0 (Zeta-Meter Inc., USA). The temperature of the samples was automatically sustained at $22^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ throughout the measurements. The results were averaged over more than three (in most cases more than five) independent measurements of separately prepared samples. In most of the experiments the ionic strength of the aqueous phase was equal to 10^{-3} M. We used the Smoluchowski formula [12,14,15] to relate the electrophoretic mobility with the droplet ζ -potential.

The size of the emulsion droplets was measured either by means of dynamic light scattering in *Zetasizer IIC* equipment (immediately before or after the EPM measurement), or separately by means of Malvern 4700C equipment (Malvern Instruments, Ltd.).

3. Experimental Results and Discussion

3.1. Emulsions stabilised with nonionic surfactants. We measured the ζ -potential of xylene droplets stabilised by blends of the nonionic surfactants Tween 20 and Span 20, mixed at different ratios. The total surfactant concentration was 10^{-4} M and the water phase contained 10^{-3} M NaCl in all these samples. The results are shown in Fig. 1. As seen from the figure, the oil droplets have significant ζ -potential in the presence of nonionic surfactants. The magnitude of the potential decreases as the concentration of the water soluble surfactant (Tween 20) increases. These results do not support the idea that the hydroxyl ions adsorb specifically at the polyoxyethylene chains of the nonionic surfactant, because the ζ -potential decreases in magnitude with increasing the concentration of the polyoxyethylene chains (note that the molecules of Span 20 have no polyoxyethylene chains).

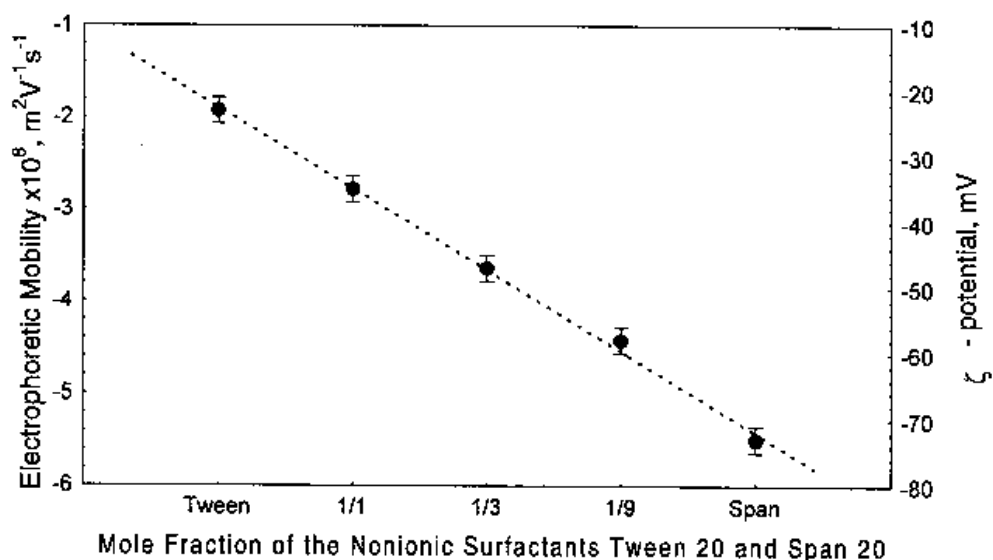


Fig. 1. Measured electrophoretic mobility and ζ -potential of xylene droplets as a function of Tween 20/Span 20 ratio at pH=6, ionic strength 10^{-3} M, and total surfactant concentration 10^{-4} M.

To clarify further the role of the surfactant oxyethylene chains we carried out experiments on emulsion droplets stabilised with ultra-pure nonionic surfactant $\text{C}_{16}(\text{OE})_8$ at different surfactant concentrations (the ionic strength was 10^{-3} M, pH = 6). The results from these experiments are

presented in Fig. 2. One sees that the increase of the surfactant concentration leads to a decrease in the magnitude of the droplet ζ -potential. These results also reject the idea that the charges are due to hydrogen bonding at the polyoxyethylene of the nonionic surfactants.

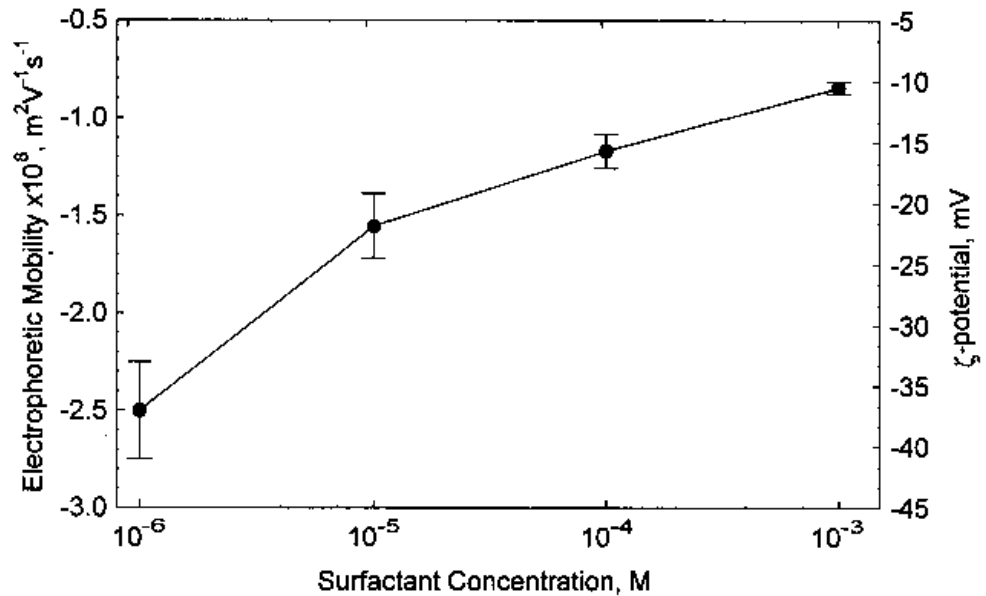


Fig. 2. Measured electrophoretic mobility and ζ -potential of xylene droplets as a function of $\text{C}_{16}(\text{EO})_8$ concentration at pH=6 and ionic strength 10^{-3} M.

Results from thin liquid film experiments [16,17] showed that emulsion films stabilised with Span 20 and Tween 20 at low ionic strength are rather thick (see Fig. 3). This large film thickness could be explained by the action of a long-range electrostatic repulsion between the film surfaces. These experimental observations confirm the importance of the electrostatic interactions for the stability of emulsions.

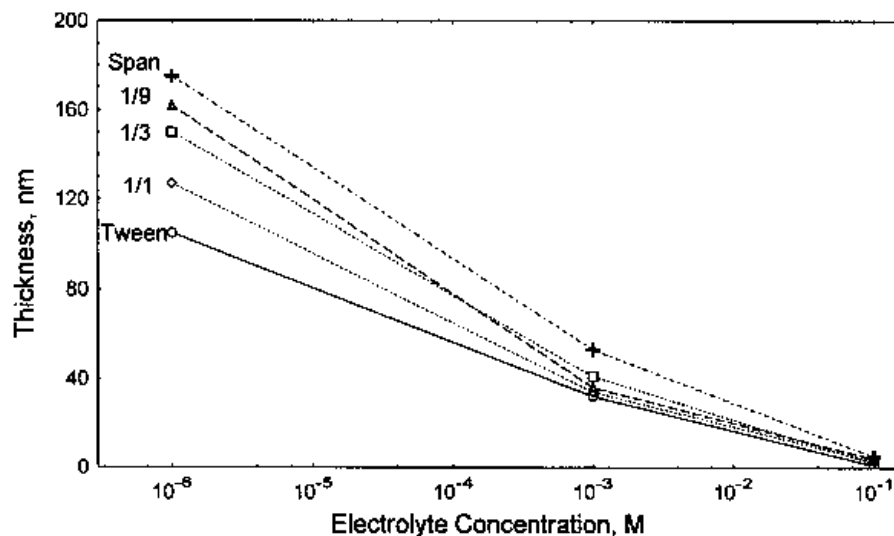


Fig. 3. Thickness of water emulsion films between xylene phases as a function of the NaCl concentration at different Tween 20/Span 20 ratios. Total surfactant concentration - 10^{-4} M, pH=6.

The results presented above suggest that the hydrogen bonding to the polyoxyethylene chains of the surfactants is not the major driving force of the surface charging. For that reason we performed systematic measurements of the ζ -potential of pure oil droplets in water, in the absence of any surfactant.

3.2. Emulsions without any surfactant. We measured the electrophoretic mobility of droplets from four non-polar oils of different chemical nature - dodecane and hexadecane (aliphatic hydrocarbons), xylene (aromatic hydrocarbon), and perfluoromethyldecalin (saturated fluorocarbon), under identical experimental conditions (pH = 6, 10^{-3} M NaCl in the aqueous phase) - see Table 1. In spite of the different chemical structure and composition of these oils, we obtained for all emulsions practically the same electrophoretic mobility: $(-4.1 \pm 0.4) \times 10^{-8} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$, and ζ -potential: $-55.3 \pm 5.0 \text{ mV}$. This result indicates that the magnitude of the surface charge depends mostly on the composition of the aqueous phase, while the nature of the non-polar phase is of secondary importance.

Table 1. Measured electrophoretic mobility and ζ -potential of droplets of different non-polar oils at pH=6 and 10^{-3} M NaCl in the aqueous phase.

Type of oil	Electrophoretic mobility $\times 10^8$ ($\text{m}^2\text{V}^{-1}\text{s}^{-1}$)	ζ -potential (mV)
Xylene	-4.44 ± 0.40	-60 ± 5
Dodecane	-4.29 ± 0.52	-58 ± 7
Hexadecane	-3.77 ± 0.59	-51 ± 8
Perfluoromethyldecalin	-3.85 ± 0.59	-52 ± 8

To elucidate further this point, we performed experiments with xylene droplets at variable pH and NaCl concentration in the aqueous medium. These emulsions were produced by the heating and cooling method, ensuring the best purity of the samples. At constant ionic strength 10^{-3} M, a strong dependence of the electrophoretic mobility on the acidity of the aqueous phase was observed (Fig. 4). Very large in magnitude negative surface potential was registered at high pH.

We performed systematic experiments in order to check five alternative hypotheses about the origin of the negative ζ -potential at the oil-water interface: (i) adsorption of hydroxyl ions at the interface; (ii) adsorption of other negative ions (e.g., Cl^- or HCO_3^- ions); (iii) negative adsorption (depletion) of positively charged ions (e.g., hydrogen ions); (iv) orientation of the water molecules in the vicinity of the oil phase; (v) adsorption of ionic surfactant molecules due to contamination initially dissolved either in the oil or in the water phase - see Ref [18] for details.

The experiments showed [18] that the adsorption of hydroxyl ions at the oil-water interface is the most probable mechanism for the negative interfacial charging. Numerical calculations (the solid curve on Fig. 4) allowed to estimate the energy of specific interaction of an hydroxyl ion with the interface $\Phi = -25 kT$ [18]. The value of the obtained specific interaction energy appears reasonable, having in mind that the hydrogen bond between OH^- ion and water molecule belongs to the so called "strong hydrogen bonds" with energy of about $60 kT$ per one bond [19].

A qualitative molecular explanation of the specific adsorption of hydroxyl ions to the oil-water interface was suggested in Ref. [18]. It is well known that a large fraction of the H-bonds between the water molecules are broken in the bulk aqueous phase due to the molecular Brownian motion. On the other hand, the thermodynamic analysis of the temperature dependence of the oil-

water interfacial tension shows that the water molecules are more ordered at the interface than in the bulk [3]. Therefore, the specific adsorption could result from more pronounced hydrogen bonding of the OH^- ion with the ordered water molecules in the interfacial layer, accompanied by a respective free energy gain.

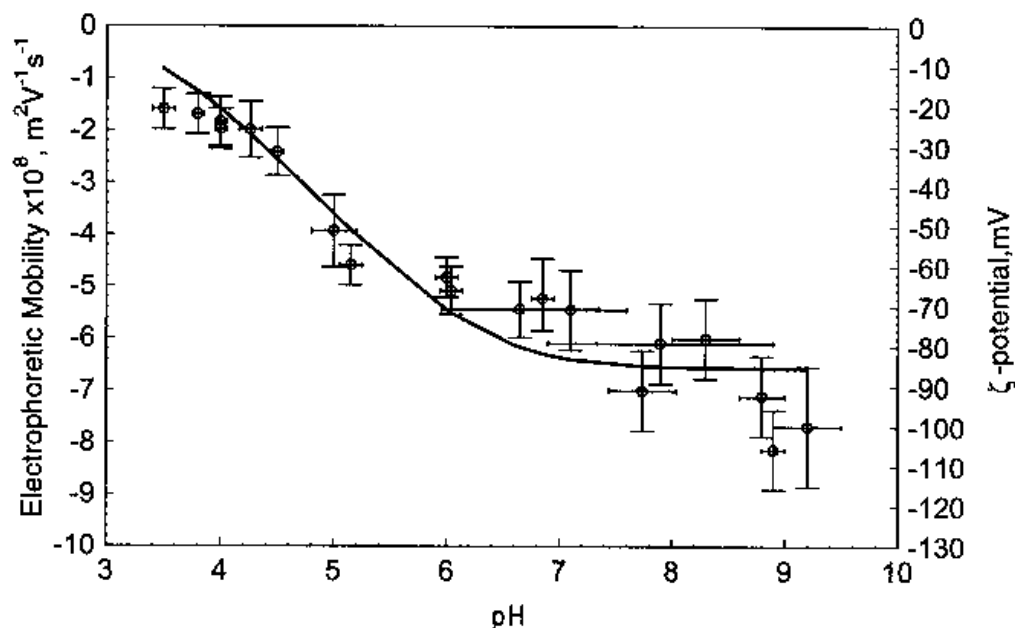


Fig. 4. Measured electrophoretic mobility and ζ -potential of xylene droplets as a function of pH at fixed ionic strength (10^{-3} M). The theoretical curve is drawn according to Grahame equation and Stern adsorption isotherm (for details see Ref. [18]).

The data in Fig. 3 and Table 1 lead to the important conclusion that the nonionic surfactants actually decrease in magnitude the inherent negative potential of the oil-water interface. Possibly this is a result of the surfactant adsorption onto the interface, which decreases (depletes) the area available for the adsorption of OH^- ions. More detailed theoretical study of the effect of the type and concentration of the nonionic surfactant is under a way.

4. Conclusions

The experiments with emulsion droplets from four different non-polar oils showed that the measured ζ -potential is within -50 to -60 mV in the absence of any surfactant, and does not depend on the oil type (pH = 6 and ionic strength 10^{-3} M of the aqueous phase). The specific adsorption of hydroxyl ions is the most probable reason for the process of surface charging.

The experiments with emulsion droplets covered by nonionic surfactants showed that the inherent negative potential of the oil-water interface decreases in magnitude when polyoxyethylene chain surfactants are adsorbed. In other words, the nonionic surfactants modify the electrostatic potential at the oil-water interface, rather than create it as thought previously.

The obtained results confirm the important role of the electrostatic interactions for the properties of emulsions stabilised with *nonionic* surfactants, which was revealed in previous studies [5,8,16-18]. One could expect that the phenomena discussed above are similar in origin to the phenomena at the *air-water* interface [20,21] and in thin foam films [22,23].

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