

# Charging of Oil–Water Interfaces Due to Spontaneous Adsorption of Hydroxyl Ions

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Received October 23, 1995<sup>®</sup>

The electrophoretic mobility of oil droplets, dispersed without any surfactant in the aqueous phase, was measured. Four different oils were studied: xylene, dodecane, hexadecane, and perfluoromethyldecalin. Special precautions were undertaken to avoid artifacts caused by the presence of surfactant impurities. The results show that the oil droplets are negatively charged and the magnitude of their  $\zeta$ -potential strongly depends on pH and the ionic strength of the aqueous phase. The electrophoretic mobility is almost independent of the type of specific nonpolar oil. Series of experiments were performed to check different hypotheses about the origin of the spontaneous charging of the oil–water interfaces. The results lead to the conclusion that hydroxyl ions, released by the dissociation–association equilibrium of the water molecules, adsorb at the oil–water interface. The specific adsorption energy was estimated to be  $25kT$  per ion ( $kT$  is the thermal energy). The molecular origin and the implications of this phenomenon are discussed. The  $\zeta$ -potential decreases in magnitude when poly(oxyethylene) chain nonionic surfactants are adsorbed at the interface.

## 1. Introduction

The properties of any interface are greatly influenced by the presence of ionic charges. The spontaneous charging of dielectric *solid* surfaces, in contact with polar liquids (e.g., water), is explained either by desorption of ions from the surface or by specific adsorption of ions from the liquid phase.<sup>1–5</sup> The charges often arise from adsorbed amphiphilic molecules which consist of hydrophobic tails and ionic hydrophilic heads. The surfactant molecules adsorbed at *fluid* interfaces (e.g., air–water or oil–water) play a crucial role in the stabilization of foams and emulsions.<sup>5–7</sup> In several studies however, spontaneous charging of oil–water interfaces was detected in the presence of *nonionic* surfactants whose molecules are not ionizable.<sup>8,9</sup> To explain this fact, it was proposed that hydroxyl ions can adsorb specifically at the interface covered with nonionic surfactant molecules, due to “hydrogen bonding at the ether-oxygens of the polyoxyethylene chain” of the surfactant.<sup>9</sup> 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 discovered<sup>10–12</sup> that the interface between water and nonpolar oil could possess substantial negative charge even in the absence of any surfactant. For instance, Carruthers<sup>10</sup> measured the electrophoretic mobility (EPM) of octadecane droplets, as well as of several octadecane derivatives containing different polar groups. He found that some qualitative relationship can be delineated between the dipole moment of the oil molecules and the EPM of the oil drops, but quantitative correlation was not established. In all cases, a strong pH dependence of the EPM was observed. Dickinson<sup>11</sup> extended Carruthers' experiments and discussed the possible source of the negative surface charge (see below). Taylor and Wood<sup>12</sup> carried out measurements of the electrophoretic mobility of decalin droplets and estimated the effect of different corrections (ion cloud relaxation, surface conductivity, and droplet phase viscosity) in Smoluchowski equation for calculating the  $\zeta$ -potential from the measured EPM. Their estimates showed that the contribution of these corrections was negligible. In most of these studies the authors presumed that the origin of the negative charge at the pure oil–water interface was the specific adsorption of hydroxyl ions from the aqueous phase. Meanwhile, measurements of the electrophoretic mobility of air bubbles in water demonstrated that the air–water interface has an electrical potential similar in sign and magnitude.<sup>13–17</sup> The charge of the air–water interface is high enough to be able to stabilize in some cases free aqueous films without any surfactant.<sup>18</sup>

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<sup>®</sup> Abstract published in *Advance ACS Abstracts*, March 1, 1996.

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In spite of the experimental evidence of negative charging of the oil–water interface, and the importance of this phenomenon for colloid behavior and stability, the origin of the charge is by no means well understood.<sup>19</sup> The only argument used to support the adsorption of hydroxyl ions as a source for the interface charging is the strong pH dependence of the measured EPM. As discussed below, other mechanisms could also predict such strong pH dependence. One obvious example is the specific adsorption of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions that may be present in the aqueous phase due to the dissolution of  $\text{CO}_2$  from the atmosphere.

In order to understand the nature of the charges at the oil–water interface, we carried out a systematic study of the role of different factors (oil type, acidity and ionic strength of the aqueous phase, etc.) on the electrophoretic mobility of oil droplets dispersed in an aqueous medium. Recently developed laser-scattering instruments for measuring EPM (like the *Zetasizer IIC* equipment used in our experiments) allow increased accuracy, because the measurement is faster and the result is averaged over many emulsion droplets. To improve reproducibility we developed experimental procedures which ensured minimal contamination of the studied emulsions and droplets of smaller diameter. All of our measurements confirmed the presence of appreciable negative charge at the oil–water interface, whose magnitude strongly depended on pH. Different series of investigations definitely lead to the conclusion that the charges originate from the hydroxyl ions which adsorb at the oil–water interface. The data were interpreted by using Stern's adsorption isotherm yielding a reasonable value for the adsorption energy of  $25kT$  ( $kT$  is the thermal energy).

The article is organized as follows: In section 2 the materials and methods for emulsion preparation and analysis are described. In section 3 the experimental results are presented and discussed. The conclusions are summarized in section 4.

## 2. Materials and Methods

**2.1. Materials.** The water for the experiments was obtained from Milli-Q Organex system (Millipore) designed for water purification from organic contaminations. Four different non-polar organic liquids were used as oil phases: xylene, dodecane, hexadecane, and perfluoromethyldecalin. The xylene phase was p.a. grade product, which was additionally purified by passing through a glass column filled with chromatographic adsorbent<sup>20</sup> (Florisil). Hexadecane (Sigma) and perfluoromethyldecalin (Rhône-Poulenc S. A., commercial name Flutec PC-7) were also purified by means of Florisil adsorbent before preparing the emulsions. Dodecane (Sigma) was used without further purification. The water and oil phases were pre-equilibrated for more than 24 h before preparing the emulsion and performing the EPM measurement (see below). The sodium chloride (Merck product) was heated at 500 °C for 6 h to remove organic impurities. The sodium hydroxide and hydrochloric acid, used for adjustment of pH of the aqueous solutions, were p.a. products, used without further purification. In some experiments the nonionic surfactant hexadecylpoly(oxyethylen)-8,  $\text{C}_{16}(\text{OE})_8$  (ultrapure brand, Nikkol, Japan), was used.

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

**2.2. Methods for Emulsion Preparation.** The electrophoretic experiments can be performed relatively easily with surfactant stabilized emulsions, but great experimental difficulties were encountered in the absence of surfactants. These difficulties are mainly caused by the rapid creaming and

coalescence of the emulsion droplets. In order to increase the reliability of the data, two alternative procedures for emulsion preparation were used.

The first procedure was close to the standard method for preparation of surfactant containing emulsions. The purified and presaturated liquid phases were mixed by a rotating blade laboratory homogenizer at approximately 3000 rpm. Some of the xylene emulsions and all dodecane, hexadecane, and perfluoromethyldecalin emulsions were dispersed in this way. Disadvantages of this method were the relatively big size ( $\geq 1 \mu\text{m}$ ) and substantial polydispersity of the oil droplets. As a result the emulsions creamed and coalesced rapidly (within several minutes) which made the measurements difficult and not very well reproducible. In addition, the metal parts of the homogenizer, which came in contact with the emulsion during its preparation, could not be cleaned with chromic acid and presented a possible source of contamination.

In order to improve the accuracy of the measurements and to ensure higher purity of the system, we developed another method that produced finely dispersed, evenly sized xylene droplets. After the pure xylene and water phases were brought into contact, the mixture was heated in a thermostat at 60 °C for 1 h. Due to the increased solubility of xylene in water at higher temperatures, a small part of the xylene dissolved in the aqueous phase. Afterward, when the system was cooled down to 22 °C (the temperature at which the measurements were performed), the excess of the dissolved xylene separated in fine emulsion droplets. The measurements of the droplet size showed that the obtained emulsions had an initial droplet diameter of 100–200 nm, and the dispersion did not separate back for a few tens of minutes. The mean size of the droplets slowly increased and reached micrometer values after 5–10 min. The electrophoretic mobility measurements with these emulsions were much more reproducible than those with emulsions obtained by the homogenizer. Last but not least, this new method allowed preparation of samples of higher purity that did not come in contact with a homogenizer and were kept in a 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 concentration of the emulsion droplets (below 0.05 vol % of oil) was adjusted in every experiment by diluting concentrated stock emulsion with a well-pre-equilibrated aqueous phase. Thus, optimal conditions for the scattered light (high intensity and signal-to-noise ratio, absence of multiple scattering) were achieved. No dependence of the measured electrophoretic mobility on droplet concentration was detected. The intensity of the electric field in the cell was varied between 15 and 22 V/cm, and the results also did not depend on it. The temperature of the samples was automatically sustained at  $22 \pm 0.1$  °C throughout the measurements. The results were averaged over more than three (in most cases more than five) independent measurements of separately prepared samples.

The Zetasizer IIC equipment measures the electrophoretic mobility,  $U_E$ , of the emulsion droplets. In most of the experiments the ionic strength of the aqueous phase was equal to  $10^{-3}$  M. Therefore, in these cases the Debye screening length  $1/\kappa$  was less than 10 nm. As usual  $\kappa$  is defined by the relationship

$$\kappa^2 = \frac{e^2}{\epsilon\epsilon_0 kT} \sum_i C_i z_i^2 \quad (1)$$

where  $\epsilon_0$  is the dielectric permittivity in vacuum,  $\epsilon$  is the relative dielectric permittivity of the solvent,  $e$  is the elementary charge,  $kT$  is the thermal energy, and  $C_i$  and  $z_i$  are the concentration and the valency of the ions of type  $i$ . Since  $\kappa a \gg 1$  ( $a$  is the droplet radius), we used the Smoluchowski formula<sup>19,21,22</sup> to relate the

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**Table 1. Electrophoretic mobility and  $\zeta$ -Potential of Droplets of Different Nonpolar Oils at pH = 6 and  $10^{-3}$  M NaCl in the Aqueous Phase**

type of oil	electrophoretic mobility $\times 10^8$ ( $\text{m}^2 \text{V}^{-1} \text{s}^{-1}$ )	$\zeta$ -potential (mV)
xylene	$-4.44 \pm 0.96$	$-60 \pm 13$
dodecane	$-4.29 \pm 0.52$	$-58 \pm 7$
hexadecane	$-3.77 \pm 0.59$	$-51 \pm 8$
perfluoromethyldecalin	$-3.85 \pm 0.59$	$-52 \pm 8$

electrophoretic mobility,  $U_E$ , with the droplet  $\zeta$ -potential

$$U_E = \frac{\epsilon \epsilon_0 \zeta}{\eta} \quad (2)$$

Here  $\eta$  is the solvent viscosity.

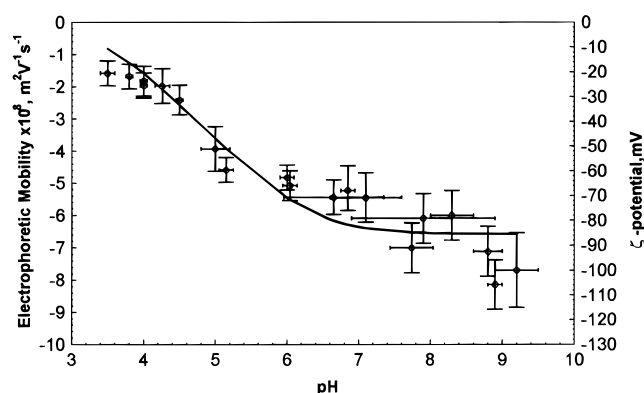
In the derivation<sup>19,21</sup> of eq 2,  $\epsilon$  and  $\eta$  are assumed to be constant. This assumption was considered by many scientists, who tried to estimate the effect of the variation of  $\epsilon$  and  $\eta$  in the vicinity of the interface. Hunter<sup>23</sup> analyzed a number of theoretical and experimental results and showed that this effect is "small under most conditions". Recently, Israelachvili<sup>24</sup> performed dynamic experiments by the surface force apparatus that directly confirmed the same conclusion for  $\eta$ . Hence, we neglected the effect of the variation of  $\epsilon$  and  $\eta$  in the analysis of our experimental data. In accordance with the conclusions of Taylor and Wood,<sup>12</sup> we also neglected the effects of the ion cloud relaxation, surface conductivity, and droplet phase viscosity. Typically, the output of an experiment was a histogram of the droplet electrophoretic mobility (or of the recalculated  $\zeta$ -potential) with a given mean value and peak half-width of about 10–15 mV. The reproducibility of the mean value when measured several times on a given sample was very good (within  $\pm 3$  mV). The reproducibility of the results from separately prepared samples (presumably of the same composition) was lower, around  $\pm 10$  mV. However, the reproducibility of the results was very poor if the xylene emulsion was diluted with *non-pre-equilibrated* solution (of the same NaCl concentration as the water phase of the emulsion) prior to the measurement. This was probably connected with the solubility of xylene in the aqueous phase, which lead to an oil dissolution process when nonequilibrated phases were brought in contact. To avoid errors from mass transfer in the samples, all phases were carefully pre-equilibrated.

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.).

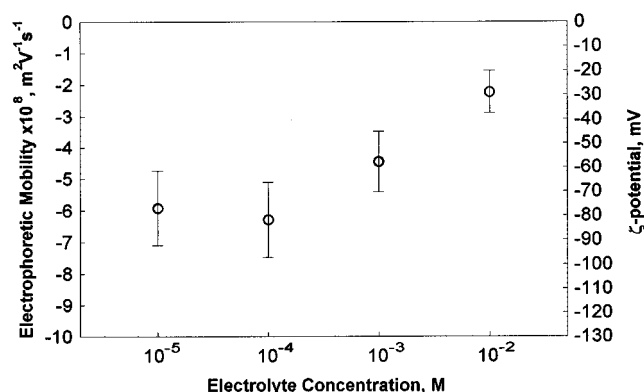
### 3. Experimental Results and Discussion

**3.1. Effect of Oil Type, pH, and Electrolyte Concentration.** We measured the electrophoretic mobility,  $U_E$ , of droplets from four nonpolar oils of different chemical nature, dodecane and hexadecane (aliphatic hydrocarbons), xylene (aromatic hydrocarbon), and perfluoromethyldecalin (saturated fluorocarbon), under identical experimental conditions (pH = 6 and  $10^{-3}$  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,  $U_E = (-4.1 \pm 0.4) \times 10^{-8} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$ , and  $\zeta$ -potential,  $-55.3 \pm 5.0$  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 oil phase is of secondary importance.

To further elucidate this point, we performed experiments with xylene droplets at variable pH and NaCl concentration in the aqueous medium. These emulsions were produced by our heating and cooling method, ensuring the best purity of the samples. At constant ionic strength, a strong dependence of  $U_E$  on the acidity of the



**Figure 1.** Measured electrophoretic mobility,  $U_E$ , and  $\zeta$ -potential of xylene droplets as a function of pH at fixed ionic strength,  $I = 10^{-3}$  M. The theoretical curve is drawn according to eqs 3 and 4.



**Figure 2.** Measured electrophoretic mobility,  $U_E$ , and  $\zeta$ -potential of xylene droplets as a function of NaCl concentration at pH = 6.

aqueous phase was observed (Figure 1). A very large magnitude in negative surface potential was registered at high pH. The observed decrease in the magnitude of  $U_E$  with the increase of the NaCl concentration (Figure 2) is usually explained with the shrinkage of the electrical double layer at high ionic strength. At lower electrolyte concentrations,  $U_E$  levels off at  $(-6.0 \pm 1.0) \times 10^{-8} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$  ( $\zeta = -80.9 \pm 14.0$  mV). It is accepted<sup>19</sup> that in this region the  $\zeta$ -potential is close to the surface potential,  $\Psi_s$ .

**3.2. Origin of the Electrical Surface Potential at the Oil–Water Interface.** The experiments with pure liquids, described above, confirm the observations reported in previous studies<sup>10–12</sup> that the oil–water interface possesses substantial electrical potential. We tried to reveal the origin of the negative  $\zeta$ -potential at the oil–water interface by checking five alternative hypotheses: (i) adsorption of hydroxyl ions at the interface; (ii) adsorption of other negative ions (e.g.,  $\text{Cl}^-$  or  $\text{HCO}_3^-$  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; and (v) adsorption of ionic surfactant molecules, due to contamination, initially dissolved either in the oil or in the water phase. All these possibilities are critically discussed below.

(i) *Adsorption of Hydroxyl Ions.* The measured strong pH dependence of the  $\zeta$ -potential suggests that the adsorption of hydroxyl ions at the oil–water interface is the most probable mechanism for the negative interfacial charging. Conversely, it is known that the close approach of an ion to the boundary between water and another phase of low dielectric constant is an energetically unfavorable process from an electrostatic viewpoint.<sup>25,26</sup> This means that ion adsorption can take place only if it is strongly

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**Table 2. Electrophoretic Mobility and  $\zeta$ -Potential of Xylene Droplets in the Absence and in the Presence of  $\text{Na}_2\text{CO}_3$  in the Aqueous Phase**

electrolyte	electrophoretic mobility $\times 10^8 \text{ (m}^2 \text{ V}^{-1} \text{ s}^{-1}\text{)}$	$\zeta$ -potential (mV)
$2.28 \times 10^{-3} \text{ M NaCl}$		
$0.36 \times 10^{-3} \text{ M NaOH}$	$-8.88 \pm 0.59$	$-120 \pm 8$
$10^{-3} \text{ M Na}_2\text{CO}_3$	$-9.03 \pm 0.37$	$-122 \pm 5$

<sup>a</sup> The acidity and ionic strength of the solutions are the same: pH = 9.8 and  $I = 2.64 \times 10^{-3} \text{ M}$ .

avored by some specific (not long-ranged electrostatic) interaction of the ion with the interface. This could be created by either the particular structure of the water molecules at the interface or the specific interaction of the ions with the hydrocarbon molecules. The first hypothesis is supported by the already established fact that the boundary water molecules are highly ordered at the interface with hydrocarbon phases.<sup>3,27</sup> By considering theoretically the boundary between water and nonpolar fluid, it has been shown<sup>28–30</sup> that the interfacial water molecules are preferentially oriented with the oxygen atoms toward the hydrophobic phase. In this respect the adsorption of the hydroxyl ions could be explained with strong dipole or hydrogen bonding of the  $\text{OH}^-$  ions with the hydrogen atoms of the interfacial water molecules.

The second hypothesis (strong interaction of  $\text{OH}^-$  ions with the oil molecules at the interface) is related to the idea of Good and Elbing<sup>31</sup> that aromatic hydrocarbons may contribute to hydrogen bonding with water at the interface. However, the fact that we have measured similar  $\zeta$ -potentials also with saturated hydrocarbons and fluorocarbon makes this hypothesis hardly believable.

(ii) *Adsorption of Other Negative Ions at the Interface.* Other negatively charged ions, present in the aqueous solutions, are  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions due to dissolved  $\text{CO}_2$  from the air. The pH dependence of the  $\zeta$ -potential can be, in principle, attributed to the different concentrations of these ions in the solution. To check the hypothesis that the surface charge might be created by the specific adsorption of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions, we performed measurements of the EPM of xylene droplets in the presence of  $\text{Na}_2\text{CO}_3$  ( $10^{-3} \text{ M}$ , pH = 9.8). The concentrations of the ions,  $[\text{HCO}_3^-] = 3.6 \times 10^{-4} \text{ M}$  and  $[\text{CO}_3^{2-}] = 6.4 \times 10^{-4} \text{ M}$ , in the solution were calculated by using data for the dissociation constants of the hydrocarbon acid ( $K_1 = 4.5 \times 10^{-7} \text{ M}$  and  $K_2 = 5.6 \times 10^{-11} \text{ M}$ ). The ionic strength was calculated to be  $I = 2.64 \times 10^{-3} \text{ M}$ . For comparison, we performed experiments at the same pH and ionic strength but in the absence of  $\text{Na}_2\text{CO}_3$ . In this case, pH and  $I$  were adjusted only by addition of NaOH and NaCl. The experimental data show (see Table 2) that the presence of  $\text{Na}_2\text{CO}_3$  practically does not influence the measured values of  $U_E$  and  $\zeta$ .

Negative chloride ions are also present in aqueous solutions of NaCl. The reported strong dependence of the  $\zeta$ -potential on pH of the solution (at constant concentration of chloride ions) shows that  $\text{Cl}^-$  are not the potential-determining ions in this case. In conclusion, the experimental results cannot be explained by the specific adsorption of  $\text{Cl}^-$  or  $\text{HCO}_3^-$  ions at the interface.

(iii) *Negative Adsorption of Hydrogen Ions.* In principle, negative potential at the interface (with respect to the bulk water phase) can be created by negative adsorption (depletion) of positively charged ions. However, simple estimations show that this explanation is unrealistic. For instance, the measured  $\zeta$ -potential at pH = 8 ( $\zeta \approx -90 \text{ mV}$ ) corresponds to excess ionic surface density on the order of  $10^{-7} \text{ mol/m}^2$  (see eq 3 below). If we assume that this surface density is due to the depletion of positively charged ions from an aqueous layer adjacent to the interface, the corresponding negative adsorption can be roughly estimated as

$$\Gamma_{\text{dep}} \approx -C_{\text{ion}} \delta$$

where  $C_{\text{ion}}$  is the bulk ion concentration and  $\delta$  is the thickness of the depletion layer. Since the bulk concentration of hydrogen ions is about  $10^{-5} \text{ mol/m}^3$  at this pH,  $\delta$  should be on the order of 1 cm to provide such large values of  $\Gamma_{\text{dep}}$ . Similarly, a thickness of  $\delta \approx 100 \text{ nm}$  is calculated for a depletion layer of  $\text{Na}^+$  ions. On the other hand, from a physical viewpoint  $\delta$  is not expected to be larger than the Debye screening length (about 10 nm). These estimates prove that the negative adsorption of positively charged ions (hydrogen or sodium) cannot explain the measured  $\zeta$ -potentials.

(iv) *Long-Range Orientation of Water Dipoles at the Oil–Water Interface.* During the last decade the interest towards the structure of the boundary interfacial layer of water molecules greatly increased due to the discovery of the long-range hydrophobic interaction.<sup>3,32,33</sup> One of the hypotheses for its explanation assumes that some *long-range* directional ordering of the water molecules (connected with a loss of entropy) takes place at the boundary with a nonpolar phase. Then the close approach of two such surfaces leads to the expulsion of some amount of oriented molecules into the bulk water phase, which is an entropically favored process.<sup>3,27</sup> If a long-range parallel ordering of polar molecules takes place in reality, it should lead to the appearance of a potential difference,  $\Psi_s$ , between the bulk water and the interface (see Figure 3). If the hydrodynamic plane of shear passes through the layer of (at least partially) oriented water molecules, this will result in a measurable  $\zeta$ -potential connected with the dipole structure close to the interface. To check this hypothesis, we measured the electrophoretic mobility of pure xylene droplets in concentrated aqueous solutions (3.2 and 5 M) of the chaotropic reagent urea. On the basis of eq 2, we calculated the same  $\zeta$ -potential, at pH = 6 and ionic strength  $I = 10^{-3} \text{ M}$ , as that in the absence of urea. Hence, the addition of a chaotropic agent, which is known to destroy the molecular network in the bulk water phase, does not change the electrostatic potential. Note, being highly hydrophilic, the urea possibly does not interfere with the ordering of the water molecules in the very close vicinity of the interface (one to several molecular layers). The obtained data suggests that a long-ranged, deeply propagating structure of water molecules is not the reason for the measured  $\zeta$ -potential. Another argument in favor of the ionic nature of the potential is the observed strong dependence on the pH of the solution (at constant ionic strength).

(v) *Contamination with Ionic Impurities.* It can be argued that negative surface charges could appear from ionic contaminations initially present either in the aqueous

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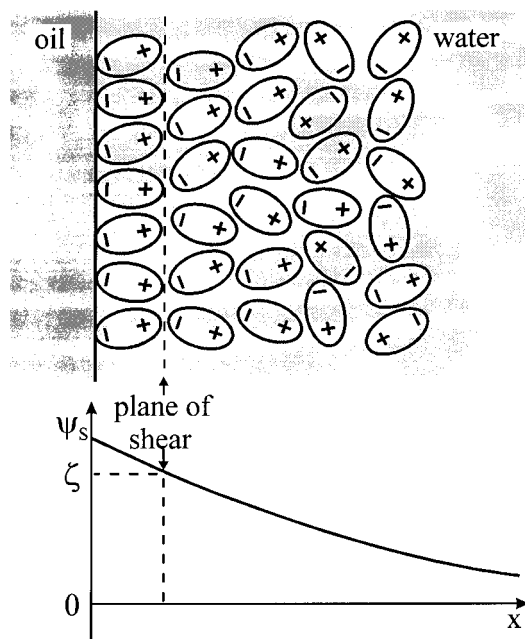
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**Figure 3.** Schematic presentation of an imaginary long-range structuring of the water molecules close to the oil–water interface which could produce electrical potential due to the molecular dipole moment (see the text). The exact position of the shear plane is not known.

or in the oil phase. We undertook a number of experimental precautions to avoid such contaminations (see also section 2):

(1) The water used for preparation of the samples was obtained from Milli-Q Organex system specially designed for removal of organic impurities. For comparison, in several experiments we used tridistilled water and obtained similar results for the EPM and  $\zeta$ -potential.

(2) The organic liquids were purified from polar contaminations by passing them through an adsorbent. In several experiments multiple elutions through fresh adsorbent were performed. Measurements with oils purified once or several times gave the same results for  $U_E$  and the  $\zeta$ -potential within the limits of the experimental error.

(3) The interfacial tension of the pure oil–water interfaces was measured by means of du Nouy ring method and was found to coincide with the literature value within the experimental error ( $\pm 0.2$  mN/m). There were no detectable changes in the interfacial tension in a time period as long as 2 h, i.e., no adsorption of surface active species was detected.

(4) The experiments with xylene emulsions, prepared by the two different methods described in section 2.3, showed very similar results. As discussed above, the second method for emulsion preparation ensured contact of the samples only with glass and Teflon that were carefully precleaned.

(5) The IR and UV spectra of the oils were recorded on Perkin Elmer 983G and Specord UV/VIS spectrophotometers, respectively. The dodecane and perfluoromethyl-decalin did not show any detectable peaks in the region characteristic for the carbonyl group. The nonpurified xylene showed a weak peak in this region (at  $1714\text{ cm}^{-1}$ ) which strongly decreased in magnitude after the first elution through the Florisil adsorbent but did not change anymore after subsequent elutions. This final very weak peak may be an overtone or combination band of the aromatic ring. These overtones are known to appear in the same region.<sup>34</sup>

In spite of the precautions taken to avoid any contamination, the possibility for the presence of traces of impurity cannot be entirely rejected. However, the reproducibility of the results obtained with different equipment and oils can hardly be explained with noncontrolled traces of contamination.

**3.3. Specific Adsorption Energy of  $\text{OH}^-$  Ion at Water–Nonpolar Oil Interface.** Since the above results strongly suggest that  $\text{OH}^-$  are the potential-determining ions, the adsorption,  $\Gamma$ , as well as the energy of specific interaction with the interface,  $\Phi$ , of these ions could be estimated.

In order to calculate the adsorption,  $\Gamma$ , from the measured  $\zeta$ -potential, we used the Poisson–Boltzmann equation and the assumption that the surface potential,  $\Psi_s$ , is equal to the  $\zeta$ -potential. This assumption is found<sup>19,35</sup> to be satisfactory at low and moderate electrolyte concentrations. The relation between  $\Gamma$  and  $\Psi_s$  is presented by the Grahame equation<sup>3</sup>

$$\Gamma = -\frac{\sigma}{e} = \frac{1}{e} \sqrt{8\epsilon\epsilon_0 kTC_{\text{EL}}} \sinh\left(\frac{ze\Psi_s}{2kT}\right) \quad (3)$$

where  $\sigma$  is the surface charge density,  $C_{\text{EL}}$  is the total electrolyte concentration, and  $z = -1$  is the ion valency.

We used the Stern isotherm<sup>1</sup> to describe the dependence of the ion adsorption upon the acidity of the aqueous phase

$$\Gamma = \frac{\Gamma_0 v_0 n_0 \exp\left(-\frac{\Phi + ze\Psi_s}{kT}\right)}{1 + v_0 n_0 \exp\left(-\frac{\Phi + ze\Psi_s}{kT}\right)} \quad (4)$$

Here  $\Gamma_0$  is the saturation adsorption,  $v_0 = 1.1 \times 10^{-22}\text{ cm}^3$  is the volume of a hydrated hydroxyl ion in the solution,<sup>3</sup> and  $n_0$  is the bulk concentration of the hydroxyl ions.

By using the least-squares method, we fitted the experimental data shown in Figure 1 by means of eqs 3 and 4 and determined  $\Phi = -25kT$  and  $\Gamma_0 = 9.8 \times 10^{-8}\text{ mol m}^{-2}$ ; see the theoretical curve in Figure 1. The value of the obtained specific interaction energy appears reasonable, having in mind that the hydrogen bond between the  $\text{OH}^-$  ion and water molecule belongs to the so called “strong hydrogen bonds” with energy  $59.4kT$  per one bond.<sup>36–38</sup> It is known that in the bulk aqueous phase fractions of the H-bonds between the water molecules are broken due to their intensive Brownian motion. Therefore, the specific adsorption could result from restrictions in the movement of the water molecules in the interfacial layer that allows more pronounced hydrogen bonding of the  $\text{OH}^-$  ion and the neighboring water molecules, accompanied by a respective free energy gain. Tools for deeper understanding and theoretical modeling of this phenomenon can be provided by the existing computer methods for studying the molecular structuring and dynamics at interfaces.<sup>39,40</sup>

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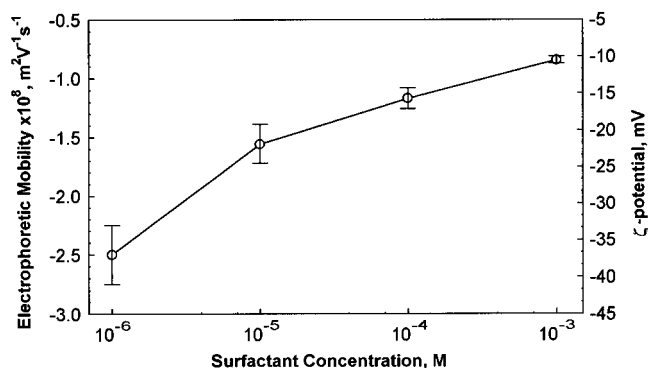
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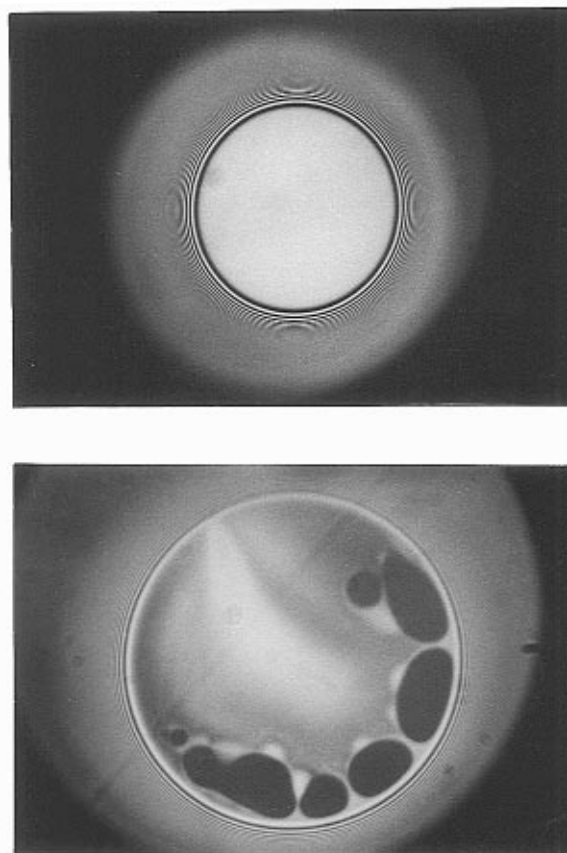
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**Figure 4.** Measured electrophoretic mobility,  $U_E$ , and  $\zeta$ -potential of xylene droplets as a function of  $C_{16}(\text{OE})_8$  concentration at pH = 6 and fixed ionic strength,  $I = 10^{-3}$  M.

**3.4. Effect of Nonionic Surfactants.** The practical application of disperse systems from pure liquids is relatively limited. Earlier it was found (see refs 41–43) that electrostatic interactions are important for emulsion systems stabilized with nonionic surfactants. To investigate how the nonionic species affect or modify the  $\zeta$ -potential of the oil–water interface, experiments with emulsion droplets stabilized with ultrapure nonionic surfactant  $C_{16}(\text{OE})_8$  were carried out at pH = 6 and  $I = 10^{-3}$  M. The results from these experiments are presented in Figure 4. The initial potential of -60 mV (Table 1) is suppressed by the presence of the surfactant on the surface. The degree of potential suppression is dependent on the emulsifier concentration. The data in Figure 1 leads to the important conclusion that the nonionic surfactants actually decrease 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  $\text{OH}^-$  ions. A more detailed study of the effect of the type and concentration of the nonionic surfactants is under way.

**3.5. Implications.** The studied phenomenon has diverse implications. There is no doubt that electrostatic interactions play an important role in the properties of emulsions stabilized by *nonionic* surfactants at low ionic strength.<sup>6,9,19,41–43</sup> An example of how the thickness and stability of thin emulsion films with nonionic surfactant are drastically affected by the electrostatic interactions is shown in Figure 5. Microscope photographs of circular emulsion films stabilized with nonionic surfactant Tween 20 are presented in this figure. The films are observed<sup>7,18,42</sup> in reflected monochromatic light that allows one to measure their thickness due to the interference of light from the two film surfaces. At low electrolyte concentration the films are very stable, and their thickness is above 100 nm due to the long-range electrostatic repulsion within the film (Figure 5a). At higher electrolyte concentration (0.1 M) the electrostatic repulsion is suppressed, and the films in a jumpwise manner form "black" spots of thickness below 15 nm (Figure 5b) and finally rupture. Details about the materials and methods used in these experiments are given in refs 42,43. Our work points out that the nonionic surfactants modify the electrostatic potential at the oil–water interface, rather than create it as thought previously. A more detailed analysis of the relationship



**Figure 5.** Microscope pictures of circular emulsion films stabilized with nonionic surfactant. The films are illuminated in reflected monochromatic light, which allows one to observe their thickness pattern due to interference between the film surfaces: (a) At low electrolyte concentration the film thickness is above 100 nm due to the long-range electrostatic repulsion between the film surfaces. (b) At 0.1 M electrolyte concentration the electrostatic repulsion is suppressed, and the films in a jumpwise manner form thinner "spots" of thickness below 15 nm and rupture. The diameter of the films is 300  $\mu\text{m}$ .

between the  $\zeta$ -potential of the oil–water interface and the emulsion stability will be given elsewhere.

During the last decade the strong attraction between hydrophobic surfaces in water has been widely studied by means of the surface force apparatus.<sup>3,32,33</sup> The experiments show<sup>32,33</sup> that the hydrophobic attraction is usually accompanied by electrostatic repulsion, the latter being explained either by the charged mica surface or by the adsorption of ionic surfactants used to hydrophobize that surface. Our results suggest that the electrostatic repulsion in these experiments could also originate from the adsorption of  $\text{OH}^-$  ions on the hydrophobic surfaces. Moreover, the adsorption of  $\text{OH}^-$  ions and the hydrophobic attraction (whose origin still remains unclear) are probably both connected to the specific structure of the boundary layer of water.

The spontaneous charging of the hydrophobic surfaces could as well be important for the stability of colloid systems other than emulsions. For example, it is widely accepted that the charge of the polystyrene latex particles comes entirely from ionizable sulfate groups, while the surface of the latex particles is predominantly hydrophobic. The hydrophobic regions on the surface of the particles could adsorb  $\text{OH}^-$  ions, which could contribute to the observed strong pH dependence of the  $\zeta$ -potential of polymer latex spheres. Another example to be discussed is the interaction between lipid bilayers. In several experiments an electrostatic repulsion between bilayers

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composed of electroneutral molecules was detected. The results were explained with eventual inclusion of ionic contaminations in the lipid bilayer.<sup>44</sup> Another possible explanation is that the adsorption of OH<sup>−</sup> ions on the bilayers could have some share in the creation of this electrostatic repulsion. As known,<sup>3</sup> when lipid bilayers are tangentially stressed, their hydrophobic interior becomes partially exposed to the water phase.

The experimental results described in the present study suggest that complete theoretical description (e.g., a thermodynamic one) and modeling of the oil–water interface cannot be achieved without taking into account the spontaneous adsorption of OH<sup>−</sup> ions. Although the bulk concentration of these ions in the aqueous phase is low, their interfacial concentration can be substantially higher due to the specific adsorption. From this viewpoint theoretical studies on the mechanism of the hydroxyl ion adsorption at the oil–water (air–water) interface might be of high interest. The approach developed in ref 40, which accounts for the configuration of the boundary layers of water molecules and for the hydrogen bond formations, seems to be the most adequate for such an investigation.

#### 4. Conclusion

The experimental results in this study confirm the presence of negative surface charge at the water–nonpolar oil interface caused by the adsorption of hydroxyl ions. The main new conclusions from this work can be summarized as follows:

(1) The experiments with four different nonpolar oils showed that at pH = 6 and ionic strength of 10<sup>−3</sup> M the measured  $\zeta$ -potential does not depend on the oil type and

is within −50 to −60 mV. The magnitude of the surface potential strongly depends on the pH of the aqueous phase.

(2) The addition of urea (up to 5 M) and Na<sub>2</sub>CO<sub>3</sub> (10<sup>−3</sup> M) does not affect the measured  $\zeta$ -potential. These results and other arguments are used to rule out several possible hypotheses about the origin of the surface charge. All obtained results lead to the conclusion that a specific adsorption of hydroxyl ions is responsible for the process of surface charging.

(3) The data for the pH dependence of the  $\zeta$ -potential are interpreted by means of the Stern adsorption isotherm. The specific adsorption energy per ion is estimated to be equal to 25*kT*. The most probable reason for the specific adsorption seems to be hydrogen bonds formation of the hydroxyl ions with the water molecules in the boundary layer.

(4) The applied procedures for ultrapure emulsion preparation (including the original procedure for xylene-in-water emulsion production described in section 2.3) resulted in more reproducible data, and not in a disappearance of the surface potential. Thus, the negative potential due to the adsorption of hydroxyl ions appears to be an inherent property of the oil–water interface.

**Acknowledgment.** We are grateful to Professor P. A. Kralchevsky for the critical reading of this paper and for useful discussions. We are indebted to Dr. T. Dudev (Faculty of Chemistry, Sofia University) for the spectral analysis of the used oils. The nonionic surfactant was kindly provided by Professor Garti (Hebrew University, Jerusalem). This study was supported by Kraft General Foods, Inc.

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