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Electrochemically driven emulsion inversion

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Abstract

It is shown that emulsions stabilized by ionic surfactants can be inverted by controlling the electrical potential across the oil–water interface. The potential dependent partitioning of sodium dodecyl sulfate (SDS) was studied by cyclic voltammetry at the 1,2-dichlorobenzene|water interface. In the emulsion the potential control was achieved by using a potential-determining salt. The inversion of a 1,2-dichlorobenzene-in-water (O/W) emulsion stabilized by SDS was followed by conductometry as a function of added tetrapropylammonium chloride. A sudden drop in conductivity was observed, indicating the change of the continuous phase from water to 1,2-dichlorobenzene, i.e. a water-in-1,2-dichlorobenzene emulsion was formed. The inversion potential is well in accordance with that predicted by the hydrophilic–lipophilic deviation if the interfacial potential is appropriately accounted for.

1. Introduction

There are two main types of emulsions, namely oil-in-water emulsions (O/W) and water-in-oil emulsions (W/O). These are also known as Winsor I and Winsor II emulsions, respectively. The type of emulsion formed is determined by the interactions between the surfactants and the two liquids. O/W emulsions are formed with hydrophilic surfactants and W/O emulsions with lipophilic surfactants. This is known as *Bancroft's rule*. It has important consequences for the choice of surfactants to obtain emulsions with desired properties.

Bancroft's rule is very powerful; for example, a change in surfactant hydrophilicity/lipophilicity can result in a transition from one emulsion type to another [1], i.e. an inversion from W/O to O/W takes place, or vice versa. Phase inversion has for example been studied by heating O/W emulsions stabilized by surfactants with polyethoxylate head groups. When the surfactant is heated the head group contracts and becomes more hydrophobic, and consequently the emulsion is converted from O/W to W/O [2, 3]. This is commonly known as the phase inversion temperature (PIT) method [4, 5]. There has been a large interest in phase inversions and optimum formulations, i.e. formulations where the hydrophilic and lipophilic

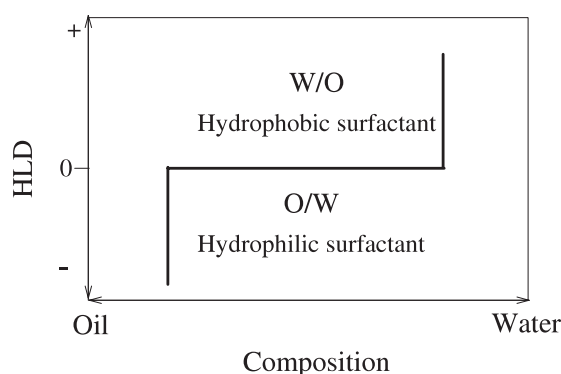


Figure 1. Schematic of the dependence of the morphology of the emulsion on the formulation (HLD) and composition of the system. The solid line represents the phase inversion boundary. The emulsion is inverted when this line is crossed.

properties of the surfactant are balanced in the system, since at this point the oil–water interface has special properties. At optimum formulation the interfacial tension is at a minimum, and consequently dispersions can be produced almost spontaneously using low energy methods for dispersion. However, at optimum formulation droplets tend to coalesce quickly, which is useful for breaking emulsions. Passing through the phase inversion point affects the morphology of the resulting emulsion [4, 6–8]. This has for example been used to make nano-emulsions, where the droplet size is in the 20–200 nm range. Nano-emulsions can for example be used to prepare polymer nanoparticles [9]. Another important application is the formation of high internal phase-ratio emulsions (HIPRE) that exceed the Ostwald critical packing ratio [10]. These are usually gel-like due to the distorted drop shape and are difficult to produce by mechanical methods.

Several quantities have been introduced for measuring the hydrophilic/lipophilic properties of a surfactant. The most common of these is the hydrophilic–lipophilic balance (HLB) introduced by Griffin in 1949 [11, 12]. Later Winsor introduced his R parameter which represents the ratio of the interaction energies between surfactant, oil and water [13]. It describes how all the formulation parameters affect the emulsion properties with a single term, and was extremely important in practice because it was a hint that the formulation could be represented somehow by a single parameter [14]. Salager *et al* have further extended these concepts into the so-called surfactant affinity difference (SAD) [15, 16] and the dimensionless equivalent hydrophilic–lipophilic deviation ($HLD = SAD/RT$) [14]. SAD and HLD are directly related to the partitioning of the surfactant between the oil and aqueous phases, which is defined by the respective chemical potentials as follows:

$$-SAD = RT \ln K = RT \ln \frac{C^w}{C^o} = \mu^{*,o} - \mu^{*,w} = \Delta\mu_{w \rightarrow o}^* \quad (1)$$

where K is the partitioning coefficient, C is the surfactant concentration and μ is the chemical potential of the surfactant in the respective phases. Figure 1 shows how the emulsion structure depends on HLD and the oil–water composition.

Equation (1) is rigorous only for non-ionic species. For ionic species the electrochemical potential, which also considers the electric potential in each phase, must be used. The electrochemical potential, $\tilde{\mu}$, is related to the chemical potential through

$$\tilde{\mu} = \mu + zF\phi \quad (2)$$

where ϕ represents the potential and z the charge of the ion. Thus, the partitioning equation takes the following form:

$$RT \ln K = RT \ln \frac{C^w}{C^o} = \tilde{\mu}^{*,o} - \tilde{\mu}^{*,w} = \Delta\mu_{w \rightarrow o}^* - zF\Delta_o^w\phi \quad (3)$$

where $\Delta_o^w\phi$ is the potential across the oil/water interface. The importance of this equation is that HLD will also depend on the potential across the liquid–liquid interface for an ionic surfactant.

Equivalently, the relation between the potential across the interface and the partitioning of an ionic species is given by

$$\Delta_o^w\phi = \Delta_o^w\phi_i^o + \frac{RT}{z_i F} \ln \frac{\gamma_i^o c_i^o}{\gamma_i^w c_i^w} \quad (4)$$

where i is the ionic species considered, $\Delta_o^w\phi_i^o$ is the standard transfer potential of the ion considered, z_i is the charge of the ion, γ_i^o , γ_i^w , c_i^o and c_i^w are the activity coefficients and concentration in the water and oil phases, respectively. In the absence of external electrodes the magnitude of $\Delta_o^w\phi$ is determined by the conditions of the equilibrium established between the two phases in contact [17, 18]. When two electrolyte solutions which are not completely miscible with each other are brought into contact, the ionic components dissolve to some extent into the other phase, depending on the hydrophilic–lipophilic balance of the ions and assuming that electroneutrality is maintained. This results in the so-called distribution potential that can be solved from equation (4) by noting that the potential across the interface is equal for any species considered. Thus, all salts present contribute to the potential across the liquid|liquid interface. Interestingly, by choosing a common partitioning ion for both phases, the potential across the interface can be controlled without external electrodes. This is particularly useful when considering reactions of an electrochemical nature taking place in emulsions where external potential control is impossible.

Electrochemistry at liquid–liquid interfaces is a powerful approach to study the ion transfer between two liquid phases and phenomena of electrochemical nature taking place at the interface formed between two immiscible electrolyte solutions. Most electrochemical techniques used for solid interfaces have been successfully applied to liquid–liquid interfaces as well. The electrochemistry and adsorption chemistry of surfactants have also been studied at polarizable liquid|liquid interfaces. Kakiuchi *et al* have reported Marangoni type movements and emulsification in the vicinity of the transfer potential, which was attributed to an electrochemical instability related to simultaneous adsorption and partitioning [19–21].

The main point of this paper is the extension of the HLD concept to include the interfacial potential difference when ionic surfactants are involved. Electrochemistry at liquid|liquid interfaces is used to characterize the partitioning behaviour of sodium dodecyl sulfate (SDS) between 1,2-dichlorobenzene and water. Furthermore, it is shown in a simple experiment that phase inversion in an emulsion can be brought about by changing the interfacial potential using potential-determining salts. The phase inversion was followed by conductometry as described previously [22], and coincided closely with the transfer potential of the surfactant, which is discussed in relation to the chemical potential and HLD.

2. Experimental details

2.1. Electrochemistry

A typical four-electrode cell configuration for the liquid|liquid interface was used [23]. The interfacial area was 0.18 cm². The potential was controlled and the current recorded using an

Autolab PGStat 100 (Ecochemie, Netherlands) potentiostat controlled by a PC. The following cell configuration was used:



where σ denotes the interface studied and x is the concentration of the ion of interest. A positive current is defined as transfer of a positive charge from the aqueous phase to the organic phase. 1,2-Dichlorobenzene (1,2-DCB) (Fluka, purum), LiCl (Merck, p.a.), tetraphenylarsonium chloride (TPAsCl) (Aldrich, USA), tetrapropylammonium chloride (TPrACl) (Fluka, purum) and SDS (Fluka, Ultra) were used without further purification. MQ-treated water was used throughout. Tetraphenylarsonium tetrakis(4-chlorophenylborate) (TPAsTPBCl₄) was prepared as described elsewhere [24].

Cyclic voltammetry was measured at sweep rates of 6, 12, 25, 50, 75 and 100 mV s⁻¹. The concentrations were 0.1 mM of TPrACl and 0.1, 0.28, 0.4, 0.55 and 0.7 mM of SDS. The base electrolytes were 10 mM LiCl in water and 5 mM TPAst in 1,2-DCB. Positive feedback was used throughout to compensate for the iR drop.

2.2. Emulsion inversion

A series of aqueous solutions containing 0.175 M SDS and 0.018, 0.035, 0.053, 0.070, 0.088, 0.105, 0.123, 0.140, 0.158, 0.175, 0.193 or 0.210 M TPrACl was prepared. The emulsions were prepared by vigorously mixing 5 ml of each solution with 5 ml of 1,2-DCB with a magnetic stirrer bar. The conductivity of each emulsion was recorded with an Orion 150 conductivity meter.

3. Results and discussion

3.1. Electrochemistry

To our knowledge 1,2-dichlorobenzene has not been used before for liquid|liquid interfaces, and therefore a few comments are merited. 1,2-DCB was used instead of the commonly used 1,2-dichloroethane, since a stable emulsion could not be obtained with the latter using SDS. The dielectric constant of 1,2-DCB is 9.93 [25], and hence similar to that of 1,2-DCE (10.36) [25]. The cyclic voltammogram of the base electrolyte window is shown as a solid line in figure 2. The size of the polarizable window, i.e. the potential region where only a small current is observed, is comparable to that of 1,2-dichloroethane, and therefore we assume that the positive end of the window is limited by the transfer of Li⁺ from the aqueous to the organic phase and the negative end by the transfer of TPAst⁺ from the organic to the aqueous phase, as has been observed for 1,2-DCE. The TPAst electrolyte solution prepared in 1,2-DCB is clearly more resistive than in 1,2-DCE due to the greater viscosity, leading to greater difficulty of compensating for the iR drop adequately. Typical values for the iR compensation were approximately 6–7 kΩ.

The voltammograms recorded with 0.1 mM TPrACl added to the aqueous base electrolyte are shown in figure 3 at sweep rates of 6, 12, 25, 50, 75 and 100 mV s⁻¹. The transfer of the TPrA⁺ ion is observed as a positive peak at 408 mV on the forward scan (negative to positive), and the back transfer as a negative peak at 338 mV on the back scan. Thus, the apparent transfer potential is $\Delta_o^w \phi_{\text{TPrA}^+} = 373$ mV. The difference in diffusion coefficients in the aqueous and organic phases has been neglected here since its contribution is small. The peak separation is approximately 70 mV at all scan rates, which differs from the 60 mV expected for a reversible reaction. The difference is believed to arise from poor compensation of the iR drop due to the

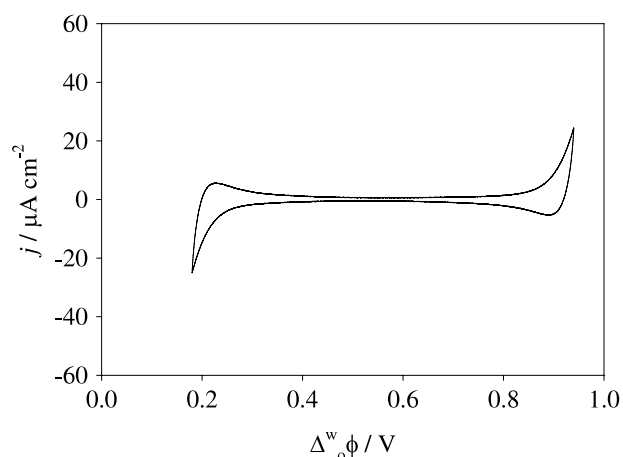


Figure 2. Cyclic voltammogram of 10 mM LiCl(w) and 5 mM TPAsk(1,2-DCB). The sweep rate was 25 mV s^{-1} . The polarizable window where only a small current flows is limited by the transfer of Li^+ at the positive end and TPAs^+ at the negative end.

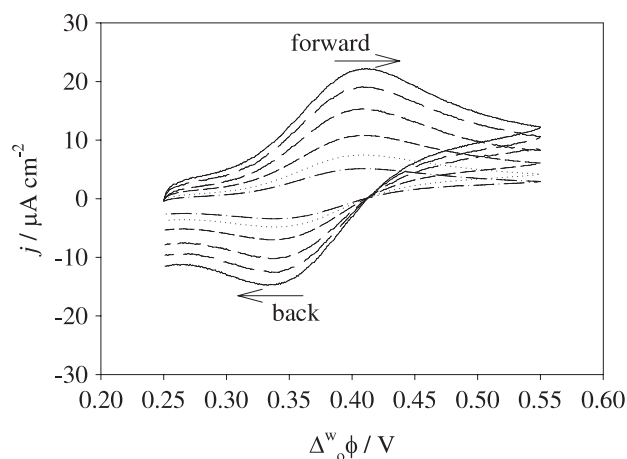


Figure 3. Cyclic voltammograms showing the transfer of 0.1 mM TPrA⁺ with the standard base electrolytes at sweep rates of 6, 12, 25, 50, 75 and 100 mV s^{-1} .

resistivity of the organic 1,2-DCB solution. The diffusion coefficient was calculated using the Randles-Ševčík equation as $0.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

The voltammograms recorded with 0.1 mM SDS added to the aqueous base electrolyte are shown in figure 4 at sweep rates of 6, 12, 25, 50, 75 and 100 mV s^{-1} . The transfer of the DS^- ion is observed as a negative peak at 330 mV on the forward scan (positive to negative), and the back transfer as a negative peak at 405 mV on the back scan. Thus, the apparent transfer potential is $\Delta_0^w \phi_{\text{TPrA}^+} = 367 \text{ mV}$. The peak separation of approximately 75 mV was interpreted as for TPrA⁺. The diffusion coefficient was calculated using the Randles-Ševčík equation as $0.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. It is pointed out here that DS^- is a surfactant and it is expected to adsorb strongly at the interface before charge transfer occurs. Adsorption phenomena are usually observed in cyclic voltammograms as a decreased peak separation and linear dependence on the sweep rate, ν , instead of $\nu^{1/2}$ expected for a reversible reaction.

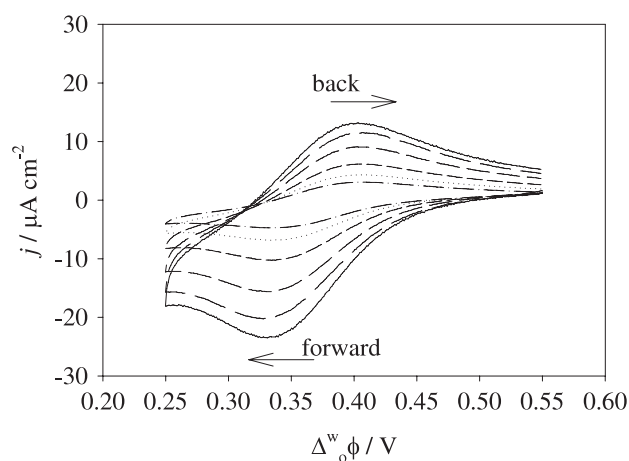


Figure 4. Cyclic voltammograms showing the transfer of 0.1 mM DS^- with the standard base electrolytes at sweep rates of 6, 12, 25, 50, 75 and 100 mV s^{-1} .

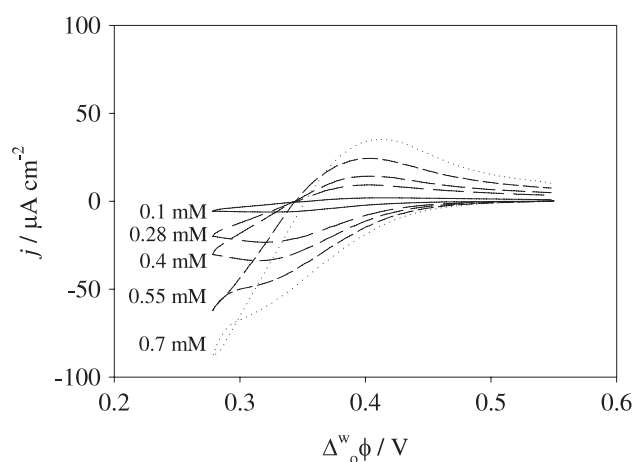


Figure 5. Cyclic voltammograms showing the concentration dependence of the transfer of 0.1 mM DS^- with the standard base electrolytes at a sweep rate of 25 mV s^{-1} . The concentrations were 0.1, 0.28, 0.4, 0.55 and 0.7 mM. At concentrations larger than 0.4 mM the voltammetric response deviates from that expected for reversible ion transfer and exceeds the diffusion limited current. This was taken as a sign of emulsification.

However, the characteristics recorded here fit a reversible mechanism well, and the adsorption step can therefore be omitted from the analysis with the sweep rates considered here. A partitioning coefficient for the dissociated salt can be obtained as the sum of the Gibbs free energies of transfer, i.e. the difference between the transfer potentials, $RT \ln K_{\text{TPrA}^+\text{DS}^-} = \Delta_0^{\text{w}} G_{\text{TPrA}^+\text{DS}^-} = F(\phi_{\text{TPrA}^+} - \phi_{\text{DS}^-}) = 578 \text{ J mol}^{-1}$. Thus, $K_{\text{TPrA}^+\text{DS}^-} = 1.3$.

Voltammograms recorded as a function of SDS concentration are shown in figure 5. Interestingly, at concentrations lower than 0.4 mM the current response is similar to that expected for reversible ion transfer. When the concentration exceeds 0.4 mM a linear increase in magnitude of the current is observed on the negative side of the half-wave potential. This increase becomes more prominent with increasing concentration and exceeds that expected from diffusion control, indicating the presence of another transport mechanism. A loop is

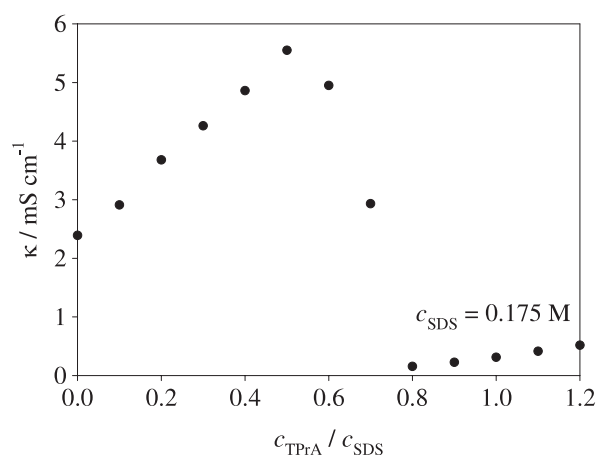


Figure 6. Conductivity of the water–1,2-DCB–SDS emulsion system as function of added TPrACl. The sudden drop in conductivity indicates the change in the continuous phase from water to oil, i.e. the inversion of the emulsion from O/W to W/O.

also observed in the voltammogram, where the current is more negative on the return sweep. Such loops are considered a typical feature for nucleation and phase formation reactions. Kakiuchi *et al* [19–21] have previously reported similar abnormalities in the region of the half-wave potential, which they showed to be related to emulsification of the oil|water interface. However, their current response was irregular which was attributed to the fusion of emulsion particles. The regular shape observed here may therefore result from more stable emulsion droplets. Furthermore, it is expected that the emulsion droplets formed are water droplets in 1,2-DCB since the surfactant partitions more into the oil at these potentials. Kakiuchi *et al* simultaneously measured the interfacial tension and noted that interfacial instability occurred despite the tension being above 23 mN m^{-1} . This was proposed to arise from the physically unrealistic negative double layer capacitance.

There is a significant difference in conductivity between O/W and W/O emulsions since the conductivity is largely determined by the continuous phase. Thus, when a phase inversion takes place from O/W to W/O the conductivity drops due to the lower conductivity of the organic solvent. Conductometry has been used to follow phase inversions [22]. Figure 6 shows the conductivity of the emulsion systems studied here as a function of the amount of added TPrACl. Before addition of TPrACl a conductivity of 2.4 mS cm^{-1} was observed, which corresponds well to the 4.9 mS cm^{-1} measured for a 0.175 M aqueous SDS solution considering the equal parts of water and oil used in the emulsion. Thus, it may be concluded that the continuous phase is water and therefore an O/W emulsion. The stability of the emulsion was good and separation of the phases occurred only after long standing. The conductivity increased with the addition of TPrACl since the salt concentration in the aqueous phase increases. It is pointed out here that TPrA^+DS^- will partition between the aqueous and organic phases, and consequently the observed increase must be primarily due to the increase in aqueous NaCl. When a sufficient amount of TPrACl has been added the conductivity of the emulsion suddenly drops. Simultaneously the emulsion became very unstable, and the phases separated within seconds after the mixing was stopped. It is noted here that the stability of an emulsion has been found to have two maxima on each side of $\text{HLD} = 0$ due to the lowered interfacial tension closer to $\text{HLD} = 0$; however, in the inversion region ($\text{HLD} = 0$) the emulsion becomes unstable due to fast coalescence of droplets [22, 26, 27].

Further addition of TPrACl induced a moderately stable emulsion with low conductivity. The low conductivity was attributed to the inversion of the original O/W emulsion to a W/O emulsion.

The relation between the potential across the interface and the partitioning of any ion in the system is given by equation (4). In addition to the activity coefficient, ion pairing and micellation need to be considered to calculate quantitative information. In the concentration range used here this task is difficult. There are, however, several qualitative features that can be deduced. When only Na^+ and DS^- are present the potential will be far more positive than the transfer potential of DS^- . Then, when TPrA^+Cl^- is added to the aqueous phase the potential becomes more negative and the concentration of DS^- in the organic phase increases following the partitioning of TPrA^+DS^- . When a sufficient amount of TPrA^+Cl^- has been added the surfactant concentration in both phases is equal and phase inversion takes place. This occurs when the ratio between TPrA^+ and DS^- is approximately 0.7. A partitioning coefficient of 2.5 is obtained if it is assumed that inversion takes place when the ratio of surfactant in each phase is 1. It compares favourably to the 1.3 calculated from the cyclic voltammograms.

The thermodynamic justifications of both Bancroft's rule and the HLD concept have a rather practical basis, since partitioning studies are tedious and time consuming. The strength of the electrochemical approach is that the measured potentials are directly related to the partitioning energies of the surfactant between the oil and water phases. Additionally, electrochemistry at liquid|liquid interfaces can be used to study adsorption processes at oil-water interfaces. Thus, it is anticipated that the electrochemical measurements can give a detailed view of the energetics involved in inversion of emulsions, and as shown by Kakiuchi *et al* [19–21] such measurements may also give detailed information on emulsification mechanisms.

For any emulsion system, the choice of the right emulsifier is very crucial. Several types of surfactant can be used. The ability to make systematic and controlled changes in the polarity of non-ionic surfactants has been considered as a major advantage over ionic surfactants which can be controlled to only a limited extent [8]. However, controlling the interfacial potential by using potential-determining ions in emulsion is a very effective means to adjust the partitioning of a surfactant. A mere change of 60 mV in the interfacial potential results in a change of the partitioning coefficient by one order of magnitude. This is likely to have far reaching consequences for creating and breaking emulsions simply by using salts which affect on the interfacial potential.

The effects of salts like NaCl on HLD and phase inversion [1, 28] have previously been studied. Such hydrophilic salts act by changing the activity coefficient of the surfactant in the aqueous phase through ionic screening and salting out. Consequently, the partitioning coefficient and HLD are changed, leading to phase inversion. However, a salt with two hydrophilic ions has only a minor influence on the potential across the oil-water interface. In contrast, salts that strongly influence the interfacial potential commonly have one hydrophilic and one lipophilic ion, and it is the partitioning of these ions that sets the potential. Thus, the effect of adding a salt with two hydrophilic ions is phenomenologically different from the use of potential-determining ions.

4. Conclusions

The concept of a generalized formulation variable (HLD) has been extended to include the electrical potential present across an oil-water interface, that must be accounted for when ionic surfactants are considered. In other words, the hydrophilic-lipophilic balance of an ionic surfactant depends on the interfacial potential and therefore on the other salts present in the

system. Inversion of a SDS stabilized emulsion was demonstrated using tetrapropylammonium chloride to control the interfacial potential drop. The electrochemical characteristics of the surfactant measured at the polarizable oil–water interface were found to correlate to the phase inversion as predicted at $HLD = 0$, i.e. optimum formulation.

While an organic phase with moderate dielectric properties had to be used to render the electrochemical measurements possible, the same principles of electrochemical equilibrium apply also to less polar solvents. In this case ion-pairing in the organic phase becomes more important.

Acknowledgment

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