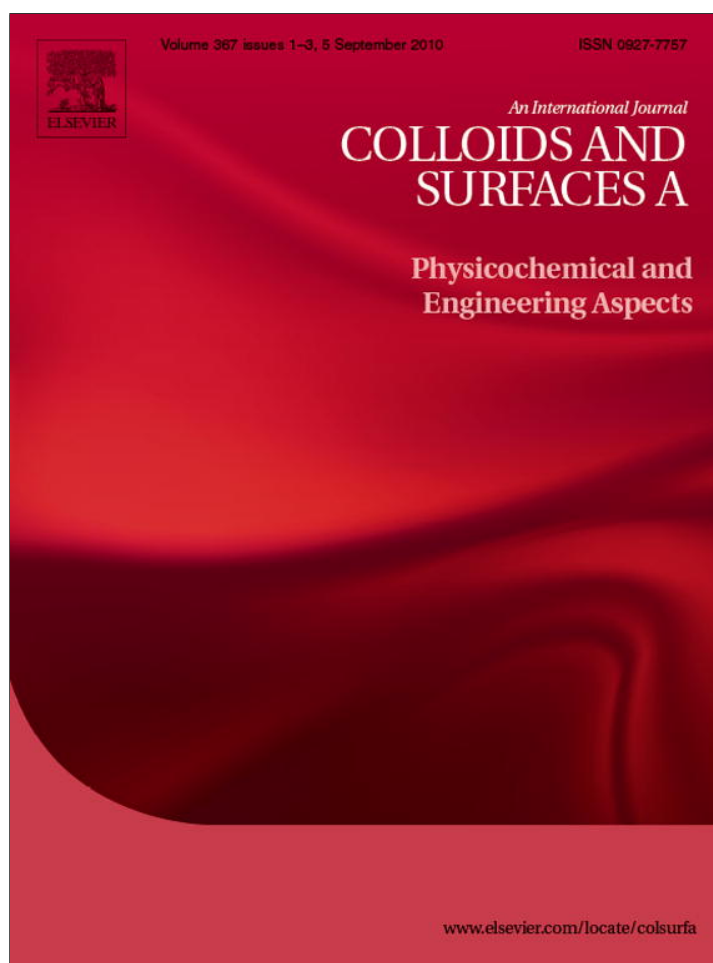


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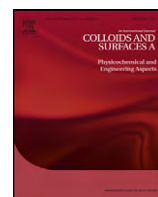
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The effect of the hydrocarbon–water interface structure on the behavior of an emulsion stabilized with dodecanephosphonic acid

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ABSTRACT

We studied the phase transition of petroleum ether/water/n-dodecanephosphonic acid (DPA) from W/O to W/O/W emulsion when the neutralization degree (nd) of dodecanephosphonic acid (DPA) with NaOH was changed. We concluded that a phase transition from W/O emulsion to W/O/W emulsion occurs when $nd \approx 0.47$ due to a change in the structure of the polar layer at the oil/water interface from a tightly hydrogen-bonded layer to a less compact layer formed by $-PO_3H_2$ and $-PO_3H^-$ groups in favor of an inversion. The W/O/W emulsion is probably caused by a partition of acid molecules in the water droplets interface inside the oil droplets, and monosodium phosphonate molecules at the external interface of oil droplets.

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1. Introduction

Phosphonate surfactants are derivatives of n-alkane phosphonic acids ($C_nH_{2n}PO_3H_2$), which are diprotic. This situation allows obtaining a variety of properties derived from its neutralization degree. These properties may be employed in practical applications, and in basic studies relating to the effect of the polar head group charge on surfactant physicochemical properties. This charge may be varied from nearly zero (acting as nonionic-like surfactants) up to -2 . Several properties of phosphonic surfactants are quite different from those of common mono-charged surfactants. A review on the properties of n-alkane phosphonic acids and their salts may be found in the literature [1].

On a previous article we have studied the inversion properties of emulsions stabilized with n-alkane phosphonic acids and their sodium salts along with their dependence on the Hydrophile–Lipophile Balance (HLB) number of these surfactants [2]. Here we selected the system n-dodecanephosphonic acid (DPA)–water–petroleum ether because of the abundant information available about DPA and their sodium salts [1,3–12].

The stability map of the emulsions system (neutralization degree vs. W_0 , the water-to-surfactant mole ratio) obtained on a

previous work [2] was redrawn and is shown in Fig. 1. Neutralization degree (nd) is defined as moles of NaOH per mol of DPA, and may be varied from zero (pure DPA) to 2 (pure disodium n-dodecanephosphonate). Because of the fact that above $nd \approx 1.2$ the studied system did not change significantly [2], we have not studied the system beyond this value.

The explored system had W_0 (moles of water per surfactant mol) between 363 and 396, which is indicated with the dotted line in Fig. 1. The transformation from W/O to multiple W/O/W emulsion occurs at the neutralization degree $nd \approx 0.47$. This part of the stability map was selected because it involves a transition caused by the change in the structure of the interface; as it might be inferred in light of the properties detected in micellar solutions involving the same surfactant, as discussed below. The rest of the stability map is similar to those obtained with other surfactants.

2. Experimental

Dodecanephosphonic acid was synthesized by means of a procedure found in the literature which is described elsewhere [7]. Only bi-distilled water was used. The oil phase was petroleum ether fraction 80–100 °C, having a required HLB (HLB_{req}) of about 14 [12]. The emulsion composition was done in terms of W_0 = moles of water per mol of surfactant. The original emulsion was prepared by mixing 0.0551 g of DPA, 20 mL of water and 20 mL of petroleum ether. The mixture was then vigorously agitated with an ultrasonic generator

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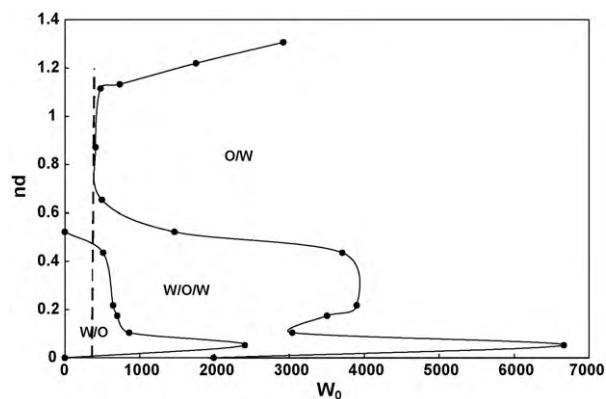


Fig. 1. Stability map of the dodecanephosphonic acid–water–petroleum ether system at 25 °C. The dotted line indicates the path explored in this work. Redrawn from data of Ref. [2].

MADA 6000 for 10 min. Then the emulsion was left to rest for 24 h before measurements were made. Samples prepared with the same components were made with the addition of different amounts of 0.181 M NaOH aqueous solution to provide different neutralization degrees (nd = moles of NaOH per mol of DPA) between 0 (no NaOH added) and 1 (i.e., $C_{12}H_{25}PO_3HNa$).

The systems were put into graduated tubes to determine the volume of the emulsion. Then, the pH was measured with a millivoltmeter and pH-meter CRIBABB and a Broade and James combined glass electrode. Finally, the emulsion was separated from the remaining solution and its viscosity measured with an AND vibro viscosimeter SV-10. A sample was studied with a Nikon E200 POL microscope, photographed and the size distribution of droplets was determined with a computer program (Pixcavator IA).

To determine the phase inversion temperature the emulsion was placed into a thermostat and the specific conductivity (κ) was measured at different temperatures with an OAKTON conductimeter and an immersion cell, calibrated as usual with KCl solution. When the temperature was changed in the range 18–95 °C, the system was maintained for 10 min at the new temperature and then the conductivity was measured. All runs were made twice. The PIT was taken as the temperature corresponding to the inflection point in the κ vs. T curve, as it is commonly done in percolation experiments.

3. Results

Fig. 2 shows the measurements of specific electric conductivity (κ) vs. temperature. Fig. 3 shows the phase inversion temperature (PIT) obtained from κ vs. T curves. The vertical line indicates the transition from W/O to a multiple W/O/W emulsion obtained from extrapolation to 25 °C giving nd = 0.47. It can be seen that the PIT is about constant with nd, except close to the inversion line at room temperature (nd ≈ 0.47), in which it drops to about 38 °C (nd = 0.435).

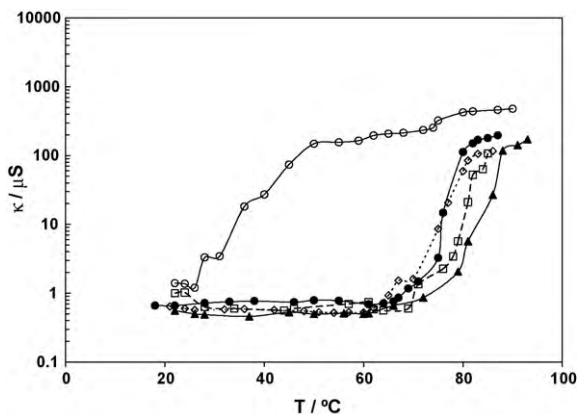


Fig. 2. Specific conductivity vs. temperature measurements for emulsions having different neutralization degrees of DPA. Neutralization degree: ●: 0; ◆: 0.053; ▲: 0.107; □: 0.174 and ○: 0.435.

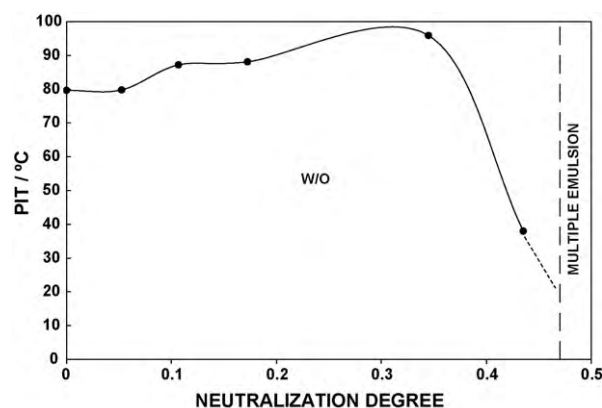


Fig. 3. Phase inversion temperature of emulsions as a function of the different neutralization degrees of DPA. The vertical dotted line is the limit between W/O and multiple emulsion at room temperature.

The PIT concept was developed by Shinoda [13,14] and shows a linear relationship with the HLB in nonionic surfactants. On the other hand, this dependence is weak for ionic surfactants [15]. It is also known that the PIT provides precise information about the various factors that affect the stability of emulsions [16].

The dependence of HLB from the surfactant on the nd values was computed with the literature HLB values [12]. The experimental dependence of HLB on nd follows the relationship: $HLB = (0.354 \pm 0.007)nd^2 + (0.59 \pm 0.1)nd + 15.20 \pm 0.01$ ($R^2 = 0.9998$) [12], with a confidence level of 0.9. Notice that the dependence is not linear.

The dependence of PIT on HLB is almost linear between nd = 0 and 0.34 and then drops as shown in Fig. 4. This linearity is characteristic for nonionic surfactants, which is the behavior of DPA [5], and indicates that the nature of the surfactant changes significantly above nd = 0.34 from that shown by typically nonionic surfactants to that of ionic ones.

Fig. 5 shows the percent of emulsion volume in the system. When this value drops below about 37.5, an inversion occurs. It can be seen that pure DPA produces the best W/O emulsion, and that the increase in the neutralization degree produces a reduction on the surfactant efficiency.

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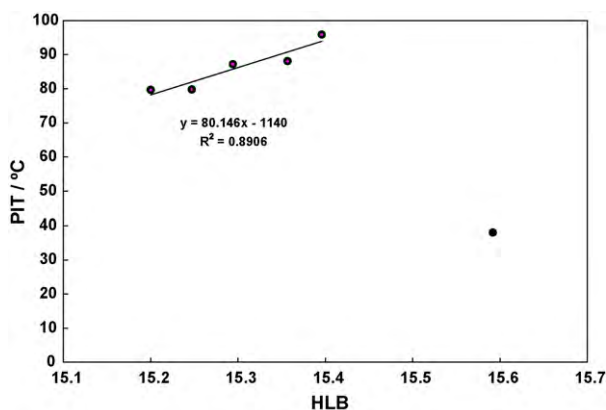


Fig. 4. Dependence of PIT on the HLB of DPA at different neutralization degrees.

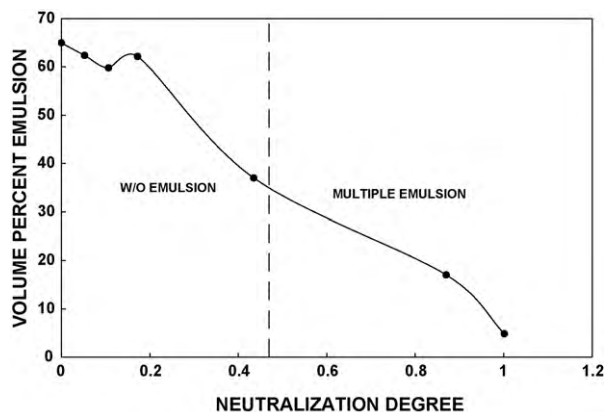


Fig. 5. Volume percent of emulsion in the system as a function of the neutralization degree. The dotted line is the limit between W/O and multiple emulsion at room temperature.

The pH values in the emulsion is almost constant up to $nd \approx 0.45$ (Fig. 6) followed by an abrupt rise. We have computed the theoretical values from the first ionization constant of *n*-dodecanephosphonic acid ($pK_{a1} = 3.98$ [17]). Notice that for $0 < nd < 1$ the surfactant solution is a buffer one showing low pH dependence on *nd*. Below the phase change border this behavior is easily seen, but there is a sudden increase on the measured pH value approaching that computed for the hydrolysis of a pure monosodium *n*-dodecanephosphonate solution.

Fig. 7 shows the size (diameter) distribution of droplets as a function of the *nd*, obtained from photomicrographs with the aid of image analysis software (Pixcavator IA). Fig. 8 shows some microphotographs of different emulsions. It can be seen in Fig. 7 that the distributions are biased as is frequent in emulsions [18]. Fig. 9 shows the dependence of the average droplets diameter and the standard deviation of the distribution on *nd*. It can be seen that the size of droplets increases from $nd = 0$ (with a low dispersity) to $nd = 0.106$, then drops to an almost constant value between $nd = 0.17$ and 0.435 . The dispersity passes through a maximum at $nd = 0.05$ and then decreases. It has a slight increase at $nd = 0.435$ near to the phase inversion. In the multiple emulsion region the size and dispersity of emulsion droplets strongly decreases. This behavior is commonly associated to a transitional inversion [18, p. 11 and 16].

We have also measured the viscosity of the emulsions (Fig. 10) showing a strong decrease between $nd = 0$ and 0.17 with an increase at $nd = 0.435$. There is a strong decrease in the multiple emulsion

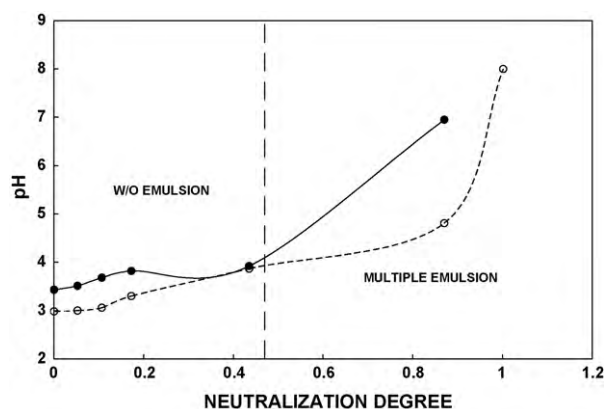


Fig. 6. Evolution of pH in the emulsion as a function of the neutralization degree. The dotted line is the limit between W/O and multiple emulsion at room temperature. Measured values: ●, computed values: ○.

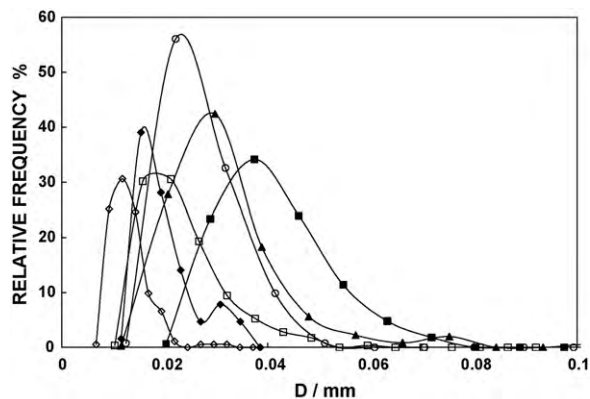


Fig. 7. Size distribution of droplets at different neutralization degrees: ◆: 0; ▲: 0.053; ■: 0.107; □: 0.172; ○: 0.435; ◇: 0.87.

domain. Since the volume fraction of the internal phase remains almost constant between $nd = 0$ and 0.17 , this reduction must be associated with the increase in droplets size and the dispersity. In the multiple emulsion zone, the reduction in size and dispersity and the change in continuous phase can be the cause of the decreased viscosity.

It may be noticed that the viscosity increases when approaching to the phase change limit and then falls. This is a characteristic of a catastrophic inversion, i.e., a phase change which may be interpreted in the light of the catastrophes theory, and may be useful for some applications [19]. The droplets size evolution is consistent with a transitional inversion. Since the transition is not reversible (as determined by titration with HCl of systems initially having disodium *n*-dodecanephosphonate as surfactant [2]), and this is a characteristic of catastrophic transitions [20], we conclude that this is probably the kind of transition observed here.

4. Discussion

The effect of the change in the neutralization degree on the kind and stability of emulsion can be followed in the preceding results. Fig. 3 shows that the PIT slightly increases between $nd = 0$ and 0.34 . Then the PIT suddenly decreases up to 38°C for $nd = 0.43$, being about 25°C for $nd \approx 0.47$.

In the literature a W/O emulsion stabilized with a hydrophobic surfactant (a sorbitol ester) was inverted by addition of a hydrophilic surfactant (lauroyl glutamate) at room temperature, a process which may be considered as similar to the partial substitution of the hydrophobic DPA by the hydrophilic monosodium dodecanephosphonate. The proportion of the hydrophilic to the hydrophobic surfactant needed to produce the phase inversion in the literature work was 12:88 [21]. The extra stabilization produced by DPA may be related with the hydrogen-bonded cohesion in the system here studied, as discussed below.

Fig. 6 shows that the percentage of emulsion in the system decreases continuously with the *nd* increase, i.e., the emulsion efficiency of the surfactant decreases in the same way.

Figs. 7–9 show that the size distributions have an approximately logarithm normal (in some cases bimodal) shape, whose average diameter of droplets first increases from $nd = 0$ to 0.106 , and then decreases remaining almost constant up to the phase transition. The standard deviation increases up to $nd = 0.05$, then passes through a minimum and rises up to the phase transition. The emulsion in the W/O/W region has the smaller average diameter and the smaller standard deviation.

The viscosity of the emulsions decreased from $nd = 0$ to $nd \approx 0.2$, then rise in $nd = 0.43$ and strongly dropped in the W/O/W region, this last behavior may be caused by the low internal phase content

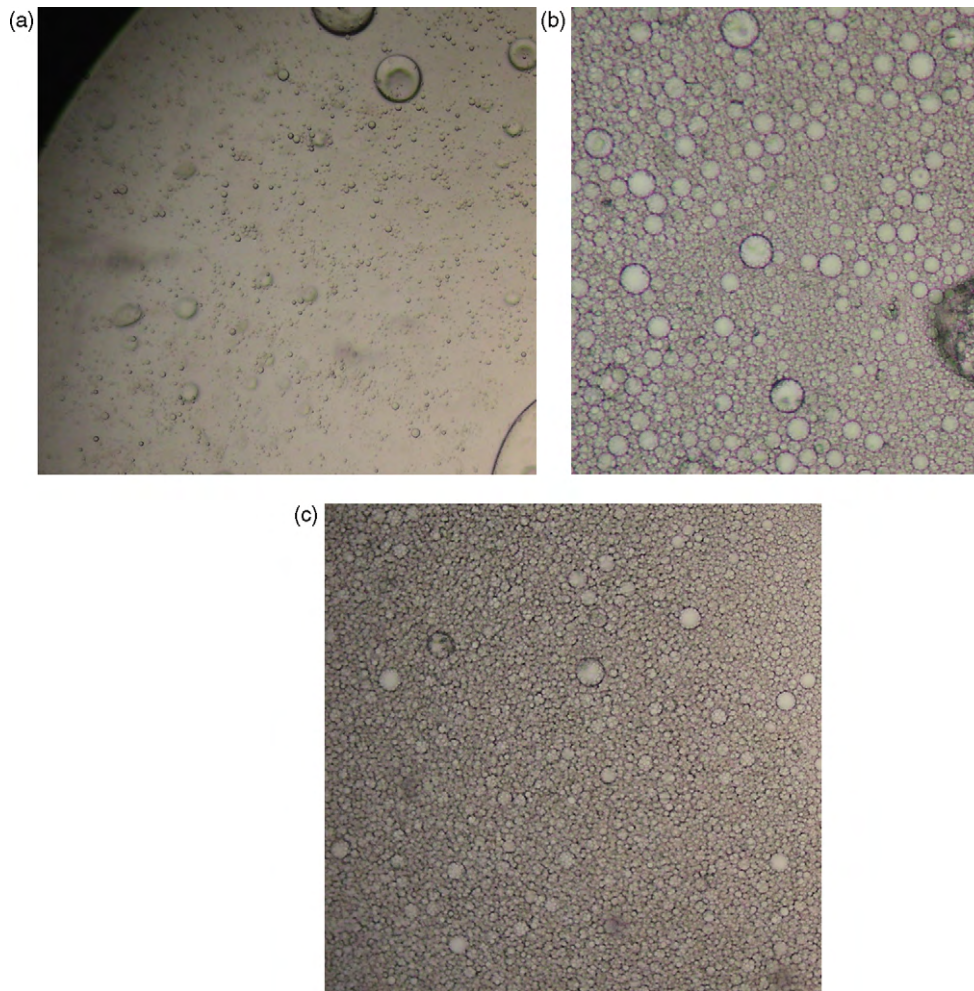


Fig. 8. Microphotographs of three emulsions with different neutralization degrees: a: $nd=0$; b: $nd=0.435$; c: $nd=0.87$.

and the low viscosity of the continuous phase [19]. The decreasing viscosity in the low nd region may be associated with the increase in the average diameter of droplets associated with the high polydispersity of the distributions. The sudden increase near the phase transition may be caused by some percolation that can produce a

network of interconnected droplets. These irregular clusters will produce a higher viscosity on the system.

Fig. 6 shows that the pH in the emulsion raises slowly when nd increases up to the phase transition point, and then rises more suddenly. This may be part of the explanation of the phase transition as detailed below.

The explanation of the inversion behavior may be related to changes in the structure of the hydrocarbon/water monolayer

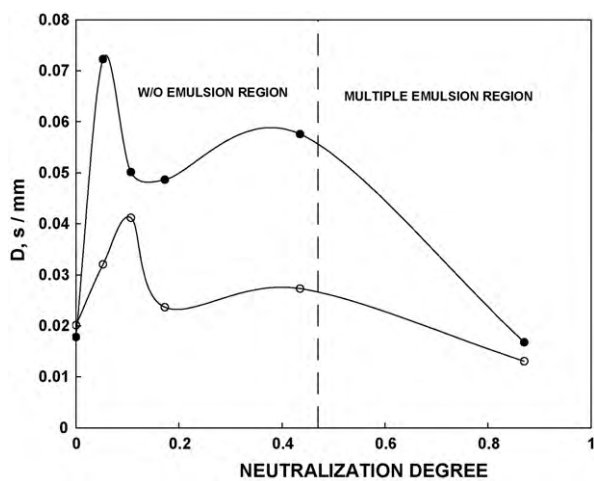


Fig. 9. Average diameter of droplets (○) and the standard deviation of the droplets' diameter (●) as a function of the neutralization degree of the surfactants. The dotted line is the limit between W/O and multiple emulsion at room temperature.

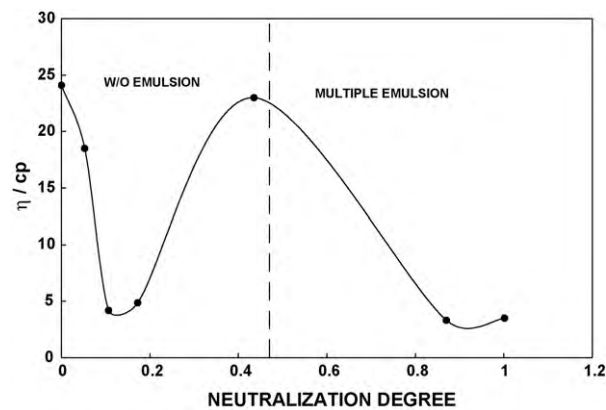


Fig. 10. Viscosity of the emulsion as a function of the neutralization degree of the surfactant. The dotted line is the limit between W/O and multiple emulsion at room temperature.

when the neutralization degree is increased. This change in the nature of the polar layer with neutralization was detected on other phosphonate systems.

The determination of the local dielectric constant at the micelle/water interface in the mixed micelles DPA–dodecyltrimethylammonium hydroxide (DTAOH) [22], indicates a change on the interface structure when the mole fraction of DPA in the surfactant mixture (without considering the solvent), $\alpha_{\text{DPA}} \approx 0.33$, i.e., when $nd \approx 1.34$. At this α_{DPA} value the composition of micelles (X_{DPA}) is equal to α_{DPA} [3]. For smaller neutralization degrees the structure of the interface is composed by phosphonic groups interconnected by hydrogen bonds, while for higher nd , the structure is composed by ionized groups. The study of the critical micelle concentration evolution with the ionization degree in aqueous DPA + DTAOH systems indicates that in micelles, the structure of the micelle/water interface changes with α_{DPA} , from scarcely ionized micelles of DPA (with the $-\text{PO}_3\text{H}_2$ groups interconnected via hydrogen bonds) to ionized micelles similar to those of other ionic surfactants above $nd = 1.2$. Additionally, the observed change is gradual between $nd \approx 0.5$ and 1, in which the proportion of DPA in micelles is higher than in the overall surfactant composition ($X_{\text{DPA}} = 0.63$, $\alpha_{\text{DPA}} \approx 0.5$). However, the composition at the air/water interface was systematically poorer in DPA than the overall surfactant mixture composition, and this effect is detected for $nd \geq 0.5$ [3]. Other surfactants that have the possibility of intermolecular hydrogen bonding have been found to have effects on micelle formation and structure [23,24].

The change from DPA to monosodium dodecanephosphonate reduces the CMC from $(4.5 \pm 2.4) \times 10^{-4}$ M [5] to $(5.8 \pm 0.1) \times 10^{-3}$ M, and to $(2.57 \pm 0.08) \times 10^{-2}$ M in the disodium salt [6]. Also, the ionization degree is high in the monosodium salt solutions, producing an increase in pH [6]. The study of the air/water structure of aqueous DPA solutions indicates that the surface below the CMC behaves as an expanded bidimensional liquid, with an area per adsorbed molecule of $A_{\text{molec}} = 0.9923 \pm 0.0001$ nm². The monolayer is non-ideal with a strong attractive interaction between surfactant molecules. However, above the CMC there is a strong desorption and $A_{\text{molec}} = 6.32 \pm 0.16$ nm², which was attributed to the energetic advantage of micelles vis-à-vis the adsorbed state, because the hydrocarbon tails–water contact is much reduced on micellization [7]. Then, a structure which minimizes the hydrocarbon tails/water contact as the oil/water interface in emulsions will strongly capture DPA molecules.

The radius of the micellized phosphonate headgroup is 0.235 ± 0.092 nm [25], which applied to the hard disk model for a bidimensional gas [26] gives an area occupied by polar headgroup of $A_0 = 2\pi r^2 = 0.35 \pm 0.13$ nm². However, in DPA crystals the area per polar headgroup was $A_0 = 0.250 \pm 0.002$ nm² [27], which probably reflects more accurately the surface occupied by a phosphonic acid group on a tightly hydrogen-bonded layer. Notice that this is about the hydrocarbon chain cross-section, namely nearly 0.20 nm².

Taking into account the above data, the possible explanation of the phase behavior in the studied system may be caused by the following transformations: with $nd = 0$, the monolayer formed by DPA molecules has a tightly polar hydrogen-bonded layer with a low value of the area per polar headgroup (a) facing the water domains. Due to the thermal agitation the hydrocarbon tails in the emulsion oil phase will be separated from each other, thus increasing the volume occupied by each chain (v), and then the Israelachvili–Mitchel–Ninham number (or packing parameter) $\text{IMN} = v/al$ [28] (l being the hydrocarbon chain length) will be higher than unity, favoring the inverted structures. Increasing nd , the value of a increases due to the electrostatic repulsion between ionized $-\text{PO}_3\text{H}^-$ groups, thus eventually decreasing the IMN number below unity and favoring planar interfaces. The sudden increase

in pH when the inversion takes place may be caused by a partial partition of the species, DPA at the interface in the water droplets inside the oil drops and monosodium salt at the external interface in the oil droplets dispersed in the water continuous matrix, as it occurs in the air/water interface of micellar systems. Since the external phase is exposed mainly to monosodium salt, the hydrolysis will be increased. This may be the explanation for the formation of a W/O/W multiple emulsion and the evolution of the emulsion proportion, along with the gradual diminution of the W/O emulsion volume in the system.

As a precedent, a highly stable W/O emulsion was made using a surfactant with the ability to form multiple hydrogen bonds, sodium 5-(1-dodecylaminocarbonyl)picolinate, and this stability was attributed to the hydrogen-bonded structure of the interface [29].

The transition followed by nonionic poly (oxyethylene) surfactants when the temperature is raised (i.e., the PIT) is O/W \rightarrow W/O while in the case of alkane phosphonic acids the transition is the inverse [30]. This indicates that the mechanism involved is different. It is not a dehydration of the polar headgroup, but probably an increase in the $-\text{PO}_3\text{H}_2$ groups ionization, causing a decrease in the IMN value and a reduction of the hydrogen-bonded network at the oil/water interface.

From $nd = 0$ to 0.10, a slight increase in a caused by the introduction of some ionized $-\text{PO}_3\text{H}^-$ groups may cause a slight increase in the IMN number, thus favoring the formation of larger water droplets by decreasing the curvature of the interface. For $nd > 0.10$, the average diameter is reduced, but the distribution is biased to the larger sizes. This may be caused by a segregation between small water droplets mainly stabilized by DPA molecules and larger ones stabilized by a variable mixture of DPA and monosodium salt, thus increasing the polydispersity.

In the light of the above discussion, it may be concluded that in some cases the particular structure of the interface may play an important role in the prediction of emulsion behavior. There are some works in the literature focusing their attention on the effect of the interface properties other than the interface tension on the stability of emulsions [31,32].

5. Conclusions

This system shows an unusual behavior, since the stability map is rather unusual; the phase transition W/O \leftrightarrow W/O/W has characteristics of a transitional phase inversion and simultaneously of a catastrophic one. However, the majority of the characteristics support the interpretation of the phase change as a catastrophic one, therefore we conclude that this is probably the case for this transition. The particular properties of this system are related to the structure change in the polar region of the surfactant monolayer at the water/hydrocarbon interface, and with the fact that at some neutralization degree, the surfactant acts as a mixture of a nonionic surfactant and an ionic one, which are partitioned between two different interfaces, one being convex to the oil phase and mainly formed by DPA, and the other to the water phase, mainly formed by ionized monosodium phosphonate molecules.

We also concluded that a phase transition from W/O emulsion to W/O/W emulsion occurs when $nd \approx 0.47$ due to a change in the structure of the polar layer at the oil/water interface from a tightly hydrogen-bonded layer to a less compact layer formed by $-\text{PO}_3\text{H}_2$ and $-\text{PO}_3\text{H}^-$ groups favoring inversion.

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