

PHASE BEHAVIOR OF pH-DEPENDENT SYSTEMS CONTAINING OIL-WATER AND FATTY ACID, FATTY AMINE OR BOTH

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Astract

The phase behavior of surfactant-oil-water systems depends upon the hydrophilic-lipophilic interaction at interface. In pH-dependent systems, the surfactant is in general a mixture of two different species: on the one hand the undissociated specie, i.e. acid or amine, which is a very lipophilic nonionic surfactant, and on the other hand the ionic salt, i.e. carboxylate or ammonium, which is very hydrophilic. A physico-chemical model that includes partitioning between phases and dissociation in the aqueous phase, is proposed and tested on systems containing long chain fatty acids or fatty amines.

Résumé

Comportement de phase des systèmes sensibles au pH, contenant de l'huile, de l'eau et un acide gras ou una amine grasse ou les deux à la fois.

Le comportement de phase des systèmes tensioactif-eau-huile dépend des interactions hydrophile-lipophile à l'interface. Dans les systèmes qui dépendent du pH, le tensioactif est en général un mélange de deux espèces différentes: une non-dissociée, tel un acide gras ou une amine grasse, qui est en général très lipophile, et l'autre, un sel ionisé, par exemple un carboxylate ou un ammonium, qui est très hydrophile. On propose un modèle physico-chimique pour rendre compte du partage entre les phases eau et huile et de la dissociation dans l'eau, et on le teste sur des systèmes qui contiennent des acides gras ou des amines grasses de longue chaîne.

Zusammenfassung

Phase Benehmen der pH-abhängigen systeme mit Oel-Wasser und Fettsauer, Fettamine oder von beiden:

Das Phase-Benehmen des Tenside-Oel-Wasser Systems hängt von der hydrophil-lipophilischen Wechselwirkung ab. Im pH-abhängigen System, das Tenside ist im allgemeinen eine Mischung von zwei verschiedenen Gattungen; auf einert Seite die nicht trennbaren Gattungen, z. Beispeil Säure oder Amine sind lipophilische nicht-ionische Tenside und auf der anderen Seite, das ionische Salz, z. Beispiel Carboxylat oder Ammonium sind stark hydrophilisch. Das physikal-chemische Model enthält die Verteilung zwischen den Phasen und der Trennung in der Wasserphase; somit wird das mit langen Fettsäure-Ketten oder Fette-Amine getestet.

1. INTRODUCTION

The oil and water phases of a typical surfactant-oil-water (SOW) system are essentially immiscible, and the presence of a third component with amphiphilic property can reduce the miscibility gap. Eventually the three components can be cosolubilized into a so-called microemulsion, which is a single phase system. From the application of the phase rule, it is known that (real ternary) SOW systems can exhibit up to three-phase behavior.

More than forty years ago, Winsor (1) established that the phase behavior of SOW systems depended not upon specific values of the formulation variables, but upon the physico-chemical situation at interface. He described the situation in terms of the ratio of the interaction energy between the surfactant and the oil phase on one side, and the interaction energy between the surfactant and the water phase on the other side. This so-called Winsor's R ratio, has been used since then as the best pedagogical tool to interpret the concept of physico-chemical formulation at interface (2).

However it is still impossible to calculate the interactions energies with accuracy and people prefer to make use of the HLB parameter, a crude empirical value that allows to locate a surfactant on a relative scale of hydrophilicity. Aside from the original definition, the HLB is today calculated for polyethoxylated nonionic surfactants as twenty times the weight fraction of the hydrophilic group in the molecule. When ionic surfactants or non polyethoxylated nonionic are concerned, Davies' relationship provides a "guesstimate", by splitting the HLB in two contributions, one for the hydrophilic group, and the other for the lipophilic one, according to the following relation (4):

$$\text{HLB} = 7 + \text{contribution of hydrophilic groups} - \text{contribution of lipophilic groups} \quad <1>$$

Since this formula will be used later in this paper, it is worth noting that the contribution of a carbon atom in a methylene group is 0.475, while the contributions of a carboxylic acid and a sodium carboxylate are respectively 2.1 and 19.1, i. e., quite different values.

In the seventies, the enhanced oil recovery application of SOW systems drove an outstanding research effort that resulted in a considerable improvement of the know how concerning the phase behavior of these systems (5-7) The concept of physico-chemical formulation was expressed in terms of numerical relationships between down-the-bench formulation variables such as brine salinity, oil alkane carbon number, temperature, and a surfactant characteristic parameter, for instance its HLB. Empirical correlations (8-9) for the attainment of an optimum formulation that produce an ultralow interfacial tension were established for both anionic and nonionic surfactants. In the past two decades the basic knowledge has advanced in two directions. On the one hand, the empirical correlations to attain an optimum formulation, have been dealt with and interpreted in a thermodynamic framework (10-11). On the other hand, the scope and range of the empirical correlations have been extended to other surfactants, other oil phases, other electrolytes, as well as mixtures of them (12-17).

Very few studies addressed the problem of pH sensitive surfactant systems, with the exception of research works related to alkaline flooding (18-21), with only two reports dedicated to the phase behavior of such systems in classical terms (22-23). In pH dependent systems, it is useful to consider that the amphiphile is made of a mixture of two surfactant species, one which is non-ionized, e.g. an acid at low pH or an amine at high pH, and the other which is the ionized counterpart, e. g. an acid salt at high pH or an ammonium salt at low pH. In this scope the overall surfactant can be viewed as the result of a mixing rule, a topic that has been already considered (24) although not with these kind of mixture, in which the partitioning (25-27) of the different species can exhibit an overwhelming importance.

2. PHASE BEHAVIOR OF SYSTEMS CONTAINING FATTY ACIDS vs. pH.

In this report, the experimental data and associated concepts are dealing with model systems that can be analyzed easily. The oil phase is a clean hydrocarbon phase, e. g., an alkane or a paraffinic/aromatic mixture, the acid is a well defined fatty acid in the C8-C16 range, and the water phase contains sodium hydroxide and eventually sodium chloride to make up the ionic strength in order to match a given salinity, that is expressed in wt.% of NaCl or NaCl equivalent (as far as the Na⁺ concentration is concerned) in the water phase. Since soaps are anionic surfactants, alcohol is added in high soap concentration systems so that a microemulsion forms instead of a solid mesophase (2, 28). In low concentration systems alcohol is not necessary, but since there is not enough surfactant to produce a three-phase optimum system, the occurrence of optimum formulation is detected through the interfacial tension minimum. The fundamental aspects of the following discussion, that is based on Cratin's approach (29), are dealt with in details elsewhere (30).

Let AcH be the non dissociated acid and Ac⁻ Na⁺ the corresponding soap specie. Subscripts "o" and "w" refer to concentrations, respectively in the oil and water phases. As may be remembered from the HLB scale, carboxylic acids (respectively soaps) have a very low (respectively high) HLB numbers. Thus their mixture can be hydrophilic or lipophilic (or indifferent, as at optimum formulation) depending upon the relative amounts of each of them.

In water, the acid is dissociated according to the following equilibrium:



with a constant :

$$K_a = \frac{[\text{Ac}_w^-][\text{H}^+]}{[\text{AcH}_w]} \quad \langle 3 \rangle$$

Where the [-] indicates the molar concentrations.

Thus, the ratio

$$\frac{[\text{Ac}_w^-]}{[\text{AcH}_w]} = \frac{[K_a]}{[\text{H}^+]} \quad \langle 4 \rangle$$

depends upon the pH. The higher the pH is, the higher the ionized fraction is and the more hydrophilic is the acid/soap mixture. The mixture HLB is supposed to be a linear function of f_i , the ionized dissociated fraction f_i :

$$\text{HLB}_{\text{mixture}} = (1 - f_i) \text{HLB}_{\text{AcH}} + f_i \text{HLB}_{\text{Ac}^-} \quad \langle 5 \rangle$$

Note that since constant K_a is typically 10^{-6} , it is obvious from formula <4> that the ionized specie exists in sizable quantity only at high pH. Thus, the surfactant (acid/soap mixture) HLB that corresponds to the optimum formulation of this particular system is attained for some value of f_i , calculated from relationship <5>. It is worth remarking that the solution depends upon HLB_{AcH} and HLB_{Ac^-} , characteristic parameters of the acid/soap pair that can be estimated from Davies' empirical relationship (4):

$$\text{HLB}_{\text{AcH}} = 9.1 - 0.475 (N-1) \quad \text{and} \quad \text{HLB}_{\text{Ac}^-} = 26.1 - 0.475 (N-1) \quad \langle 6 \rangle$$

where N is the number of carbon atoms of the fatty acid/soap.

The previous discussion applies for the water phase equilibrium. In presence of a two phase system (water/oil), some of the surfactant species can partition into the oil phase. In the present case,

it is assumed that only the non dissociated specie AcH is able to partition into the oil, as indicated in Figure 1. For the sake of simplicity of the mass balance, it is assumed that the water-to-oil ratio (WOR) is unity.

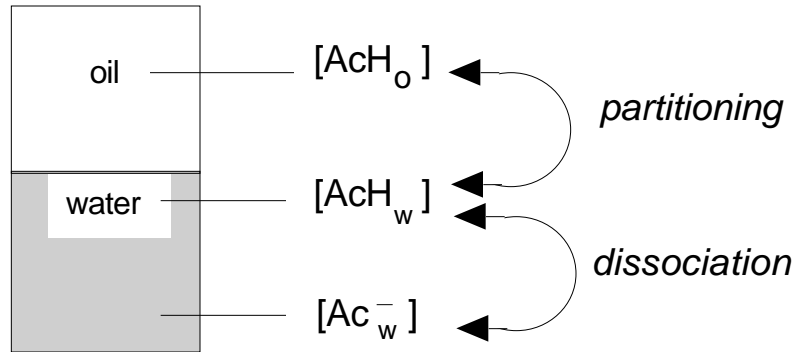


Fig. 1: Partitioning of the non dissociated acid between water and oil, and acid/soap dissociation equilibrium in the aqueous phase.

The partition coefficient of the non-dissociated acid is defined (for a WOR=1 system) by:

$$P_a = \frac{[AcH_o]}{[AcH_w]} \quad \langle 7 \rangle$$

Since P_a is typically 10^2 (30), it is obvious that neglecting the non dissociated acid that has partitioned into the oil phase can lead to a great inaccuracy. A straightforward calculation (30) allows to link the pH to the overall acid dissociated fraction f_i :

$$pH = -\log_{10}[H^+] = \log_{10} \frac{f_i}{1-f_i} + \log_{10} \frac{P_a}{K_a} \quad \langle 8 \rangle$$

where the dissociated fraction is defined as $f_i = \frac{[Ac_w^-]}{[AcH_t]}$ $\langle 9 \rangle$

in which $[AcH_t]$ is the total acid originally in the system, calculated as a concentration in water or oil, which is the same since it was assumed that WOR=1.

By combining equations $\langle 5 \rangle$ and $\langle 8 \rangle$, a relationship is attained between the pH and the overall HLB of the acid/soap mixture:

$$\frac{HLB_{mixt} - HLB_{AcH}}{HLB_{Ac^-} - HLB_{AcH}} = f_i = \frac{1}{1 + \frac{P_a}{K_a} [H^+]} = \frac{1}{1 + 10^{pH_{1/2} - pH}} \quad \langle 10 \rangle$$

where HLB_{AcH} and HLB_{Ac^-} numerical values can be calculated from relation <6> and $pH_{1/2}$ stands for the pH at which half the original acid has been dissociated, i. e., $f_i = 0.5$, which is the decimal logarithm of the ratio P_a/K_a according to equation <8>.

This can be written as:

$$\frac{HLB_{mixt} - HLB_{AcH}}{HLB_{1/2} - HLB_{AcH}} = 2 f_i = \frac{2}{1 + \frac{P_a}{K_a} [H^+]} = \frac{2}{1 + 10^{pH_{1/2} - pH}} \quad <11>$$

where $HLB_{1/2}$ is the average HLB of the acid/soap mixture with 50% of each, that can be readily calculated from equations <5> and <6> with $f_i = 1/2$, as $17.0 - 0.475 (N-1)$.

A further manipulation leads to:

$$\frac{HLB_{mixt} - HLB_{1/2}}{8.5} = 2 f_i - 1 = \frac{1 - \frac{P_a}{K_a} [H^+]}{1 + \frac{P_a}{K_a} [H^+]} = \frac{1 - 10^{pH_{1/2} - pH}}{1 + 10^{pH_{1/2} - pH}} \quad <12>$$

This expression shows that the pH-HLB plot is the same for all acid/soap pairs when referred to coordinates centered at $pH_{1/2}$ and $HLB_{1/2}$. Figure 2 exhibits the typical sigmoid aspect of the graphical representation with a buffered HLB variation (almost pH independent) near the central point at $HLB_{1/2} - pH_{1/2}$ (black dot). Figure 2 shows the HLB-pH curves corresponding to different acid/soap pairs, and indicates the associated shift in $pH_{1/2} - HLB_{1/2}$ along a line that is straight because on the one hand the variation of $HLB_{1/2}$ with N is linear according to relation <6>, and on the other hand, the logarithm of the partition coefficient is likely to change also as a linear function of N, as it does in many surfactant systems (27). When these different acid/soap pairs are used in a given physico-chemical context, i. e. with a given oil and water phases, as well as temperature, then, the optimum formulation for three-phase behavior is attained for a certain value of the surfactant characteristic parameter, for instance its HLB, that is symbolized as HLB^* .

Because the HLB scale changes from hydrophilic to lipophilic in the range 9-11, it is likely that HLB^* is near this value for most systems. This range corresponds to the region where the HLB vs. pH curve is almost vertical. Thus, the intersection of the HLB-pH curve with an horizontal line at optimum HLB^* (see frame in Figure 2) defines an optimum pH symbolized pH^* . Because of the very steep variation of HLB vs. pH in the crossing region, pH^* is actually very close to $pH_{1/2}$, which is located at the inflexion point of the curve. This is true for different acids, each of them characterized by its pH^* or $pH_{1/2}$, as shown in Table I data. Note the linear variation of these characteristic pH values with the acid chain length and the agreement between the two series of data.

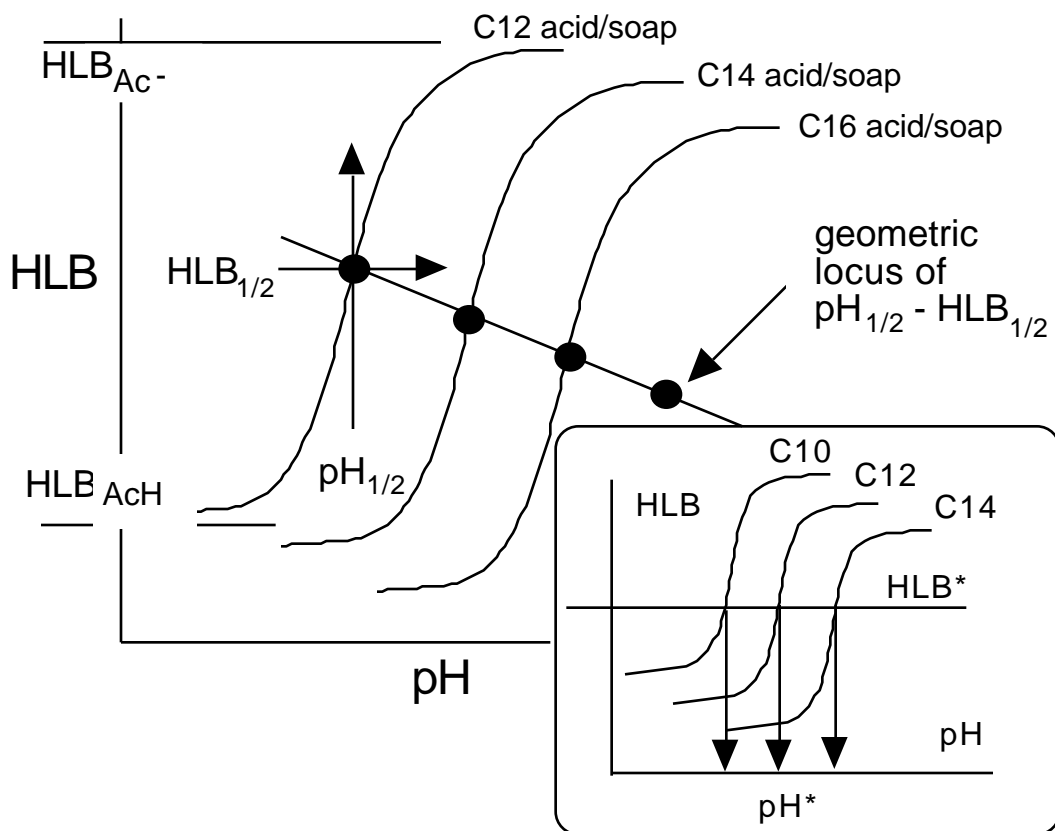


Fig. 2: Relationship HLB-pH in oil/water systems for different fatty acid/soap pairs (30)

Table I: Values of characteristic $pH_{1/2}$ and pH^* for different acid/soap pairs (30) in a system containing water, and a mixed (xylene/heptane 25/75) oil phase.

Acid N	C08	C10	C12	C14	C16	C18
$pH_{1/2}$	7,2	8,0	8,9	9,5	10,30	11,0
pH^*	7,0	7,9	8,7	9,6	10,35	11,15
P_a/K_a	$1.6 \cdot 10^7$	$7.9 \cdot 10^7$	$5.0 \cdot 10^8$	$3.1 \cdot 10^9$	$2.2 \cdot 10^{10}$	$1.4 \cdot 10^{11}$

By using relation <8> at $f_i = 1/2$, P_a/K_a can be calculated readily from $pH_{1/2}$ (see Table I). Since K_a is believed to be essentially the same for all fatty acid (with a value about 10^{-6}), then the logarithm of the partition coefficient varies linearly vs. the number of carbon atoms in the acid/soap pair, the increase in P_a being roughly a factor 2.6 per added carbon atom.

Figure 3 shows the variation of the optimum pH^* (for three-phase behavior) for a system mentioned in Table I and some other systems containing alcohol and brine instead of pure water. The symbol "eq. NaCl" means that the total Na^+ ion concentration is maintained constant by adding a proper amount of NaCl to the NaOH solution used to adjust the pH, and that the salinity is expressed

as the NaCl concentration that produces the same Na^+ concentration. In each case, the phase behavior depends upon the relative position of the pH with respect to the corresponding pH^* . If $\text{pH} < \text{pH}^*$ (respectively $\text{pH} > \text{pH}^*$) the lipophilic non-dissociated acid (respectively the dissociated soap) dominates and a Winsor II (respectively Winsor I) phase behavior is observed in which an oil base (respectively a water phase) microemulsion is at equilibrium with an excess aqueous (respectively oil) phase. In the neighborhood of pH^* a three-phase behavior is exhibited.

In Figure 3 an asterisk indicates the neutralization pH for an aqueous solution of (C12) lauric acid. It is seen that this pH is above all pH^* attained with all systems containing an oil phase and eventually alcohol. This is due to the fact that only a part of the acid needs to be dissociated for the overall HLB to attain the optimum value HLB^* according to relation <5>. Figure 3 shows that the pH^* depends also upon the nature of the oil and water (salinity) phase, as well as upon the presence of alcohol. This is consistent with the fact that HLB^* depends upon all these variable. The relative position of the three pH^* -N lines for different alcohol mixtures (triangle dots) in Figure 3 shows that a more lipophilic alcohol mixture results in a higher pH^* , an indication that a higher fraction of dissociated soap, i. e., the hydrophilic specie, is required, in perfect agreement with the trends exhibited in simple surfactant systems according to Winsor's theory (1-2, 8-9).

As a final comment it can be remarked that the slope of the optimum lines depends upon the nature of the water and oil phase, and the presence of alcohol. This is no wonder since the partition coefficient, and probably the dissociation constant as well, are affected by these variables.

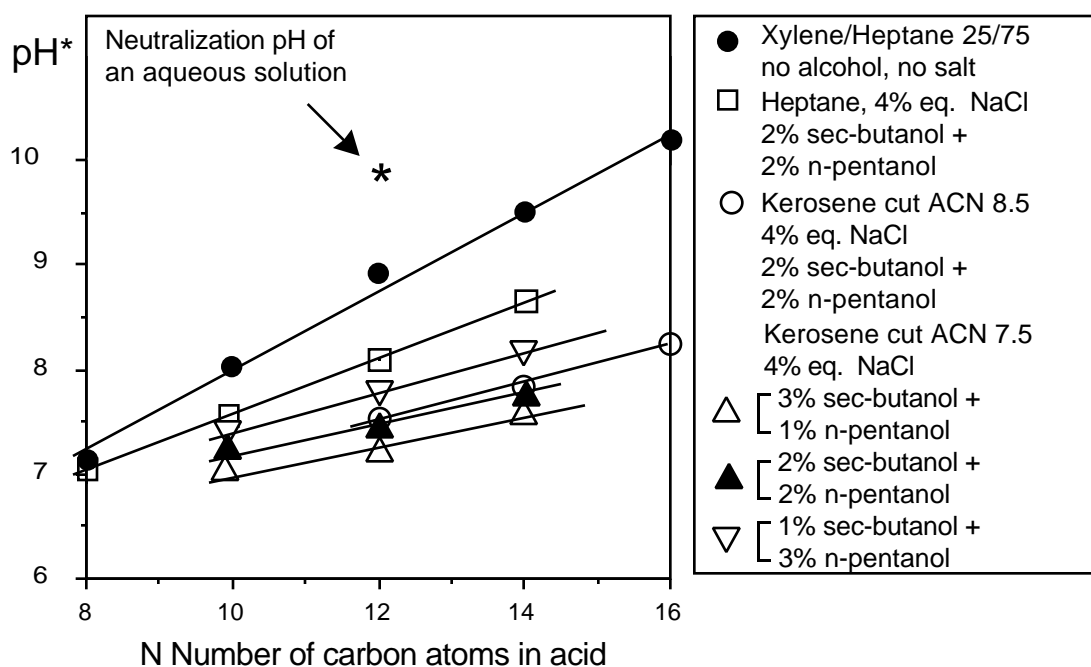


Figure 3: Optimum pH^* for different systems versus the fatty acid chain length (30).

3. PHASE BEHAVIOR OF SYSTEMS CONTAINING FATTY AMINES vs. pH.

The amine protonation equilibrium can be written in a similar fashion than the acid/soap dissociation:



with an ionization constant:

$$K_b = \frac{[\text{AmH}_w^+][\text{OH}_w^-]}{[\text{Am}_w]} \quad \langle 14 \rangle$$

where Am stands for the non-dissociated amine, AmH⁺ the ammonium ionic specie, and where subscripts w and o refer respectively to the aqueous and oil phases.

The partitioning of the non-ionized amine between the oil and water phases is written as:

$$P_b = \frac{[\text{Am}_o]}{[\text{Am}_w]} \quad \langle 24 \rangle$$

A calculation similar to the one carried out for the acid/soap systems leads to :

$$\text{pOH} = -\log_{10}[\text{OH}^-] = \log_{10} \frac{f_i}{1-f_i} + \log_{10} \frac{P_b}{K_b} \quad \langle 25 \rangle$$

with the ionized fraction define as

$$f_i = \frac{[\text{AmH}_w^+]}{[\text{Am}_t]} \quad \langle 26 \rangle$$

If the HLB of the amine/ammonium mixture is written as:

$$\text{HLB} = f_i \text{HLB}_{\text{AmH}^+} + (1-f_i) \text{HLB}_{\text{Am}} \quad \langle 27 \rangle$$

The relationship between HLB and pOH can be shown to be:

$$\frac{\text{HLB}_{\text{mixt}} - \text{HLB}_{\text{Am}}}{\text{HLB}_{\text{AmH}^+} - \text{HLB}_{\text{Am}}} = f_i = \frac{1}{1 + \frac{P_b}{K_b} [\text{OH}^-]} = \frac{1}{1 + 10^{\text{pOH}_{1/2} - \text{pOH}}} \quad \langle 28 \rangle$$

where

$$\text{pOH}_{1/2} = \log_{10} \frac{P_b}{K_b} \quad \langle 29 \rangle$$

For similar reasons than in the acid/soap case, i.e., the shape of the curve that renders equation <28> variation, pOH_{1/2} is very close to pOH*, where three-phase behavior is exhibited. Table II indicates both experimental values for two different systems. If it is assumed (30) that K_b is

approximately 4×10^{-4} , then P_b is in the 100-200 range, a value perfectly similar to the partitioning coefficient found in the acid/soap case.

As a consequence, it can be said that the acid/soap and amine/ammonium mixture exhibit exactly the same behavior, provided that the pH is taken in the first case as the ionization variable and the pOH in the second one. When $pH > pH^*$ or $pOH > pOH^*$, the ionized specie dominates and a Winsor I phase behavior is attained. When the opposite applies, a Winsor II phase behavior is exhibited.

The overall situation is illustrated in Figure 4 in which the two cases are gathered. It is worth remarking that in each case the phase behavior depends upon a critical value (pH^* or pOH^*), that has been shown to be close to the center of the sigmoid curve (equations <11> and <28>) that relates the HLB with the pH (or pOH), and that was called $pH_{1/2}$ in the acid/soap case and $pOH_{1/2}$ in the amine/ammonium one.

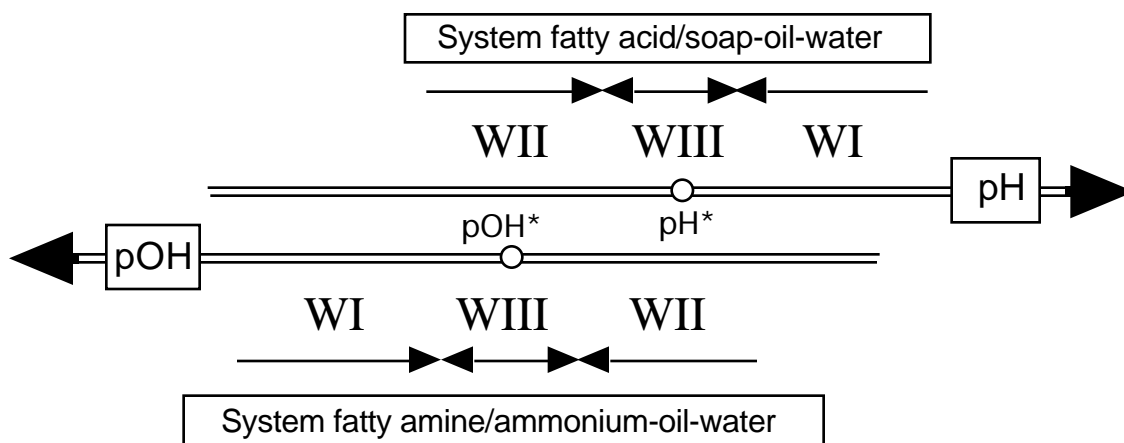


Figure 4: Phase behavior of SOW systems containing acid/soap or amine/ammonium as a function of the pH (or pOH).

Table II: Values of characteristic $pOH_{1/2}$ and pOH^* for different amine/ammonium pairs (30) in a system containing brine, heptane and 3% amyl alcohol.

Amine N - salinity	C10 - 2 % NaCl	C12 - 0,5 % NaCl
pH^*	7,5 - 7,70	7,15 - 7,22
$pOH_{1/2}$ (estimate)	6,4	6,8
P_b/K_b	3×10^6	7×10^6

The $pH_{1/2}$ and $pOH_{1/2}$ characteristic parameters depend upon both the dissociation equilibrium constant and the partition coefficient. But since the dissociation constant does not change significantly with the acid or amine chain length, the values of $pH_{1/2}$ and $pOH_{1/2}$ depend essentially upon the partition coefficient of the non-ionized specie between oil and water, the logarithm of which is known to change linearly with the number of carbon atoms in the acid/amine hydrophobe form; the (scarce) available experimental evidence (30), indicates a variation that may be expressed as:

$$\frac{dpH_{1/2acid}}{dN} = \frac{d\log_{10} P_a}{dN} = \frac{dpOH_{1/2amine}}{dN} = \frac{d\log_{10} P_b}{dN} = 0.25 \pm 0.5 \quad ??? \quad <30>$$

This is no wonder that the characteristic parameter changes linearly with the hydrophobe length, since it is the same with all other formulation parameters that enter the generalized formulation expression so-called “Surfactant Affinity Difference” or SAD, that is no more than a summation of energetic terms (10, 11, 31). The found value is however much larger than the one encountered for nonionic surfactant partitioning (27).

4. PHASE BEHAVIOR OF SYSTEMS CONTAINING BOTH FATTY ACID AND FATTY AMINE vs. pH.

When the SOW system contains both a fatty acid and a fatty amine, the phase behavior situation depends upon the relative position of the critical parameter pH^*_{acid} and pOH^*_{amine} . The three possible combinations are found in Figure 5.

In case (a), the phase behavior transition occurs for the acid-oil-water system at a lower pH than for the amine counterpart. At both extreme of the pH scale the phase behavior is opposite for both systems. As a consequence, it is expected to be WI or WII with the acid/amine mixtures, depending upon the relative amount of the ionized and non-ionized species, which depends upon the relative amount of acid and amine in the system, as well as the partitioning.

In the central region, i.e. at $pH > pH^*_{acid}$ and $pH < pH^*_{amine}$, the phase behavior is WI for both systems when they are considered separately, but when the acid and amine are mixed, the presence of both ionized species, i.e. soap and ammonium, is likely to result in a very strong interaction similar to the one exhibited in anionic-cationic mixtures with a resulting equimolecular catanionic substance (32), that is in general rather hydrophobic. Thus, the WI region vanishes and these systems exhibit a WII phase behavior at mid range pH, as will be seen later.

In case (b) the two critical pH values just coincide and the previous discussion applies for the extremes as well.

In case (c) the phase behavior is WII for both systems in the central pH region and opposite at both extremes. Thus, in the central region a WII phase behavior is likely to be exhibited for any mixture, since the eventual combination of free soap with free ammonium would result in an extra hydrophobic contribution. At the pH range extremes the situation is similar to the one in other cases, i. e., the phase behavior depends upon the relative amount of acid and amine and their partitioning.

It has been discussed in a previous section that both $pH_{1/2 acid}$ and $pOH_{1/2 amine}$ increase when the acid or amine chain length increases. Since the optimum (*) and central (1/2) values are very close, it can be said that an increase in chain length is expected to produce an increase in pH^*_{acid} , and an increase in pOH^*_{amine} , or a decrease in pH^*_{amine} . In other words an increase in chain length would displace the acid/soap transition in Figure 5 toward the right, and the amine/ammonium transition toward the left. Thus, the relative position of the two characteristic pH*s depends upon the chain length of the fatty acid and amine. It has been found (30) that with a system containing heptane, 4 wt.% NaCl brine, 2 % n-pentanol and 2% sec-butanol, case (b) corresponds to a C10-acid/C10-amine mixture, while cases (a) and (c) occur respectively for the C12, and C8 counterparts.

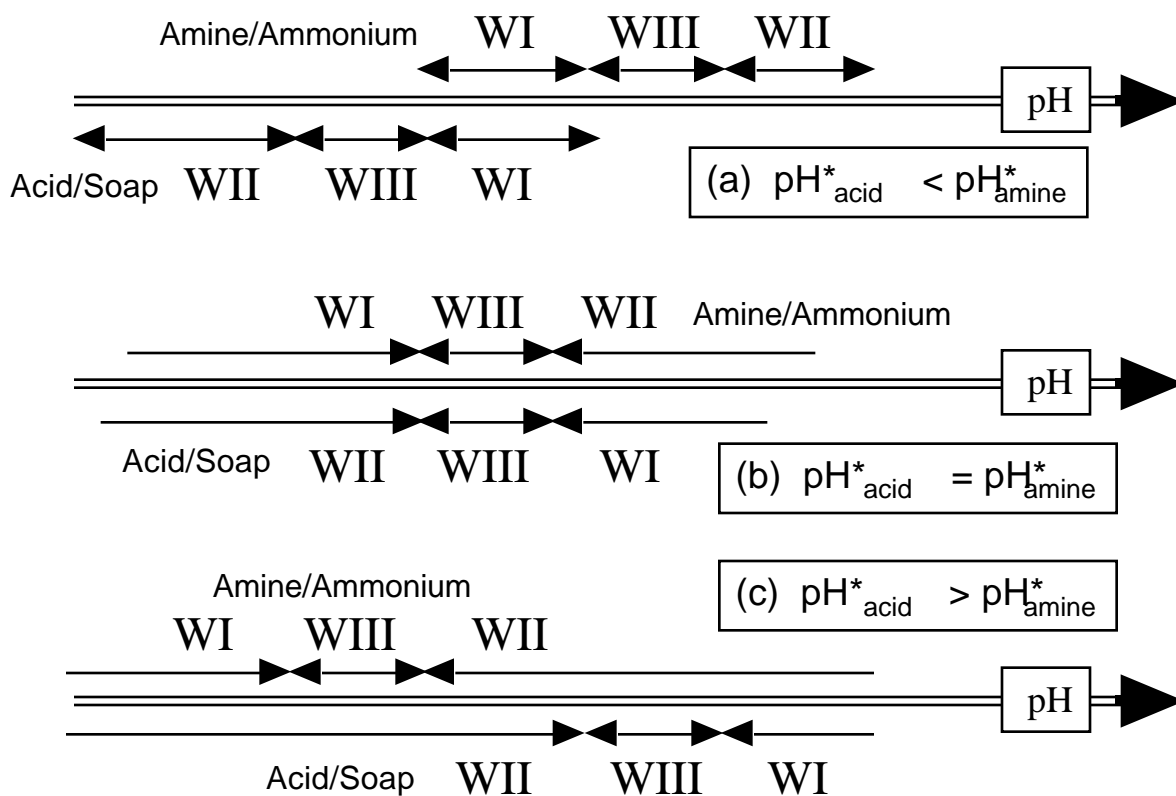


Figure 5: Comparison of the Phase Behavior of systems containing oil-water and acid/soap or amine/ammonium in different cases.

Experimental phase behavior studies are carried out for unit water-to-oil ratio systems, by changing both the pH and acid/amine relative content. Since the addition of chlorhydric acid or sodium hydroxide is required to change the pH, a zero electrolyte concentration is not feasible. Since salinity is known to affect the formulation (2, 8, 30), it should be maintained constant. In Figure 6 case, a 4% equivalent NaCl salinity is used; the HCl or NaOH added to adjust the pH is counted as equivalent NaCl (for a same molar concentration) and the salinity is adjusted to 4 wt.% by adding sodium chloride.

Figure 6 corresponds to case (a) in Figure 5, in which the central pH region ($7 < \text{pH} < 9$) exhibits a WI phase behavior for both acid/soap and amine/ammonium separated systems. However, it is seen that the WI phase behavior zone does not extend from 100% acid to 100% amine in the central region, because the ionic species soap and ammonium combine together to produce a catanionic specie that is much more hydrophobic (32) and results in a WII phase behavior.

On the other hand at low pH, the acid/soap mixture contains very little soap and it is thus rather lipophilic, while the amine/ammonium mixture, mostly ammonium, is rather hydrophilic. The phase behavior depends upon the relative amount of both of them. For instance at $\text{pH} = 4$, three-phase behavior, i. e., optimum formulation, is attained for a 50% mixture. At a lower pH, e. g. 3, the acid/soap equilibrium is no longer affected, while the amine/ammonium is still found to increase its apparent hydrophilicity. As a consequence the WI phase behavior zone extends as pH decreases. A similar trend occurs on the high pH range extreme, but this time with the soap being the specie that increases its hydrophilicity. It is believed that this continuing change beyond the optimum pH is mainly due to the effect of the partition coefficient of the non-ionized specie, the concentration of which becomes smaller and smaller in the aqueous phase as the transition pH gets farther and farther away.

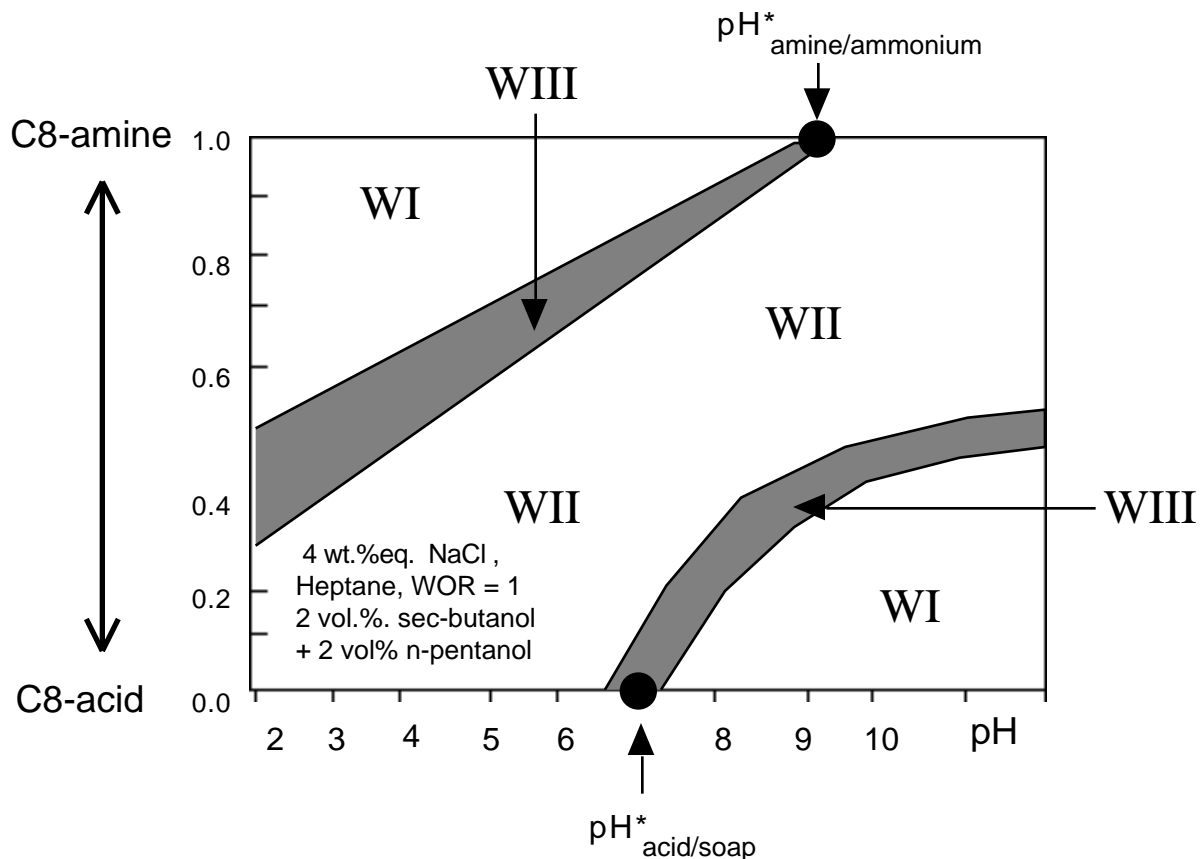


Figure 6: Phase behavior of a SOW system containing a mixture of octylamine and caprylic acid vs. aqueous phase pH and acid/amine composition

Figure 6 exhibits a complex map with quite useful features as far as applications are concerned. For instance, there is a slanted wide band of WII phase behavior, and two strips with WIII phase behavior. At pH 8 a double transition WI-WIII-WII-WIII-WI takes place from 100% amine to 100% acid. Since the phase behavior is associated with emulsion properties (33-35), this complex phase behavior is probably associated with a quite uncommon emulsion property map.

Of course the phase behavior is also affected by the oil nature, the aqueous phase salinity and the temperature (2, 8, 9) but these effects are in agreement with the general trends and they only produce a shift in actual values without changing the whole picture.

5. CONCLUSION

The phase behavior of Surfactant-Oil-Water systems in which the surfactant is pH-dependent is similar to the one attained by mixing an hydrophilic surfactant and a lipophilic one. The relative amount of each of the species depends upon the pH that drives the dissociation in the aqueous phase. However it is shown to depend also upon the partition coefficient of the non-dissociated specie between oil and water.

When acid and amine are mixed in variable-pH SOW systems the phase behavior depends upon the relative position of the characteristic pH of each separated acid-water-oil and amine-water-oil systems.

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