

Interfacial Behavior of Asphaltenes

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Asphaltenes are one of many naturally occurring materials whose chemical makeup is so ill defined that classical analytical methods used to elucidate their structure, mechanism, and activity are only partly successful. Fortunately, however, data derived from measurements of their interfacial tension as a function of pH have been employed to explain and to predict their behavior with a high degree of accuracy. Based on a general technique developed by the author, a mathematical model utilizing simple chemical reactions and equilibria has been constructed that will give quantitatively (a) the relative activities of all chemical species that result from reactions of asphaltenes with hydronium and hydroxyl ions; (b) the apparent equilibrium constants that describe these reactions occurring at the oil-water interface; (c) the fraction of each of these species present as a function of pH; (d) the effect of oxygen on the chemical nature and behavior of asphaltenes; and, (e) a foundation for a mathematical criterion for emulsion stability.

•MOST natural products have a chemical makeup so ill defined that classical analytical methods used to elucidate structure, mechanism, and activity are, at best, only partially successful. Fortunately, however, data that can be obtained from straightforward surface chemical measurements may frequently be employed to explain and to predict the behavior of many complex substances, the most notable examples being naturally occurring materials whose properties depend on pH. In recent publications, Cratin and co-workers (1, 2, 3, 4) have described the development of a general method to characterize quantitatively pH-dependent systems. This technique has been used to account for such diverse phenomena as stability of crude oil emulsions, transience of some natural products, and even the specificity of enzymatic reactions. Indeed, this general method can be used for any system whose "activity" may be determined as a function of pH. (By "activity" is meant some pH-dependent property that may be in nature and is either thermodynamic, e. g., surface and interfacial free energies, or kinetic, e. g., rates of chemical reactions.)

Having established this activity-pH relationship, one can construct a mathematical model, based on simple chemical reactions and equilibria, that will give quantitatively (a) the relative activities of all chemical species that result from reactions with hydronium and hydroxyl ions; (b) the degree to which any (or all) of these species may interact; (c) the apparent equilibrium constants that describe the reactions occurring in solution or at an interface; and (d) the fraction of each species present as a function of pH.

In this paper, the general method will be used to describe the interfacial behavior of a class of highly complex, chemically ill-defined materials, the asphaltenes. Furthermore, it will be demonstrated that correct use of the method allows one to account quantitatively for the effect of oxygen on the chemical nature and behavior of asphaltenes; and finally, it will be shown that this method serves as a foundation for a mathematical criterion for emulsion stability.

EXPERIMENT

The separation of the asphaltenes from crude oils was carried out according to the method outlined by Sachanen (5). To preserve anaerobic conditions, separations were carried out in an atmosphere of dry nitrogen, and the samples were stored away from light in airtight weighing bottles. Each solvent was sparged with dry nitrogen prior to use to remove any traces of dissolved oxygen.

A stock solution of asphaltenes was prepared by extracting approximately 5 grams of the solid with 500 ml of a hot cyclohexane-benzene mixture. When cool, the resulting solution was filtered through coarse Whatman paper into a stoppered volumetric flask. This solution was kept blanketed with a dry nitrogen atmosphere. Aqueous phases were prepared by adjustment of the pH (as determined by a Beckman pH meter, model G, of triply distilled water to desired values with 0.5 N NaOH and HCl.

Interfacial tension measurements were made with a Cenco-du Nouy tensiometer fitted with a Call ring alignment joint according to the standard procedure given, for example, in Daniels (6). Added by buret into a 100-ml beaker were 35 ml of the aqueous phase, and the du Nouy ring was immersed to ensure complete wetting. Then, 25 ml of the stock asphaltene solution were carefully discharged from a pipette on to the surfaces of the aqueous phase. (Great care was exercised to avoid turbulence; at extreme pH values, turbulence would result in the formation of emulsions and the disappearance of the interface. When this occurred, the samples were discarded.) The du Nouy ring was then raised to the interface, allowed to age for 5 min, and finally pulled up through the interfacial region. The interfacial tension was determined from a corrected dial reading.

RESULTS AND DISCUSSION

Relative Interfacial Tension versus pH

The experimentally determined values for the relative interfacial tension as a function of pH are shown in Figure 1. (For reasons that will become obvious later, interfacial tensions are expressed on a relative rather than on an absolute scale.)

A great deal of information can be gleaned from the general shape of the γ_i/γ_o versus pH curve. The fact that the interfacial tension is high in the intermediate pH region (i. e., 4 to 8) and that it falls off rapidly in both acidic and basic solutions indicates that asphaltenes are amphoteric in nature. That this is true may be shown by the following argument.

Their large degree of aromaticity and their enormous molecular weights render the asphaltenes virtually insoluble in water but somewhat soluble in organic liquids. If basic groups on the asphaltene "molecule" were present, they would be protonated at low pH values to species that, being ionic, would show some hydrophilic character. The tendency of the hydrophilic "part of the molecule" to migrate into the aqueous phase would be partially offset by the driving force of the hydrophobic "part of the molecule" to remain in the organic phase. The result would be a concentration

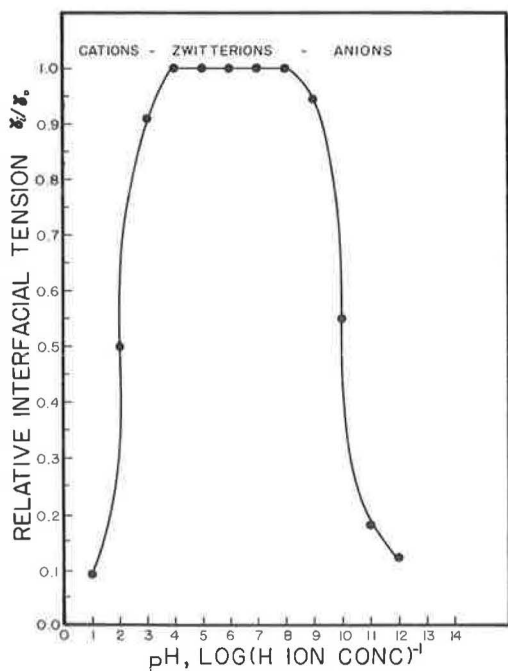


Figure 1. Experimental relative interfacial tension as function of pH (anaerobic).

buildup at the oil-water interface, thus causing a lowering of the interfacial tension—a phenomenon that is observed experimentally. This argument can be extended for regions of high pH where the asphaltenes would react with hydroxyl ions to form anionic "soaps," materials that also possess a remarkable ability to lower the interfacial tension. If this argument is valid, one can postulate the existence of a charge-neutral species (hereafter referred to as the "zwitterion") in the region of the broad, flat maximum shown in Figure 1. At low pH values, the dominant species is a positively charged moiety that we shall call the cationic species (cations). In regions of high pH, the species of greatest concentrations is a negatively charged "molecule" that we shall refer to as the anionic species (anions). Between the extreme values of γ_1/γ_0 in the region of low pH, there exists a mixed interfacial film that consists of zwitterions and cations. In the higher pH region, the interfacial film is composed of zwitterions and anions.

Mathematical Model Proposed

In order to visualize what appears to happen at the molecular level, let us suppose we have our system initially in a region of very low pH. Virtually all of the asphaltene material will have been converted to the cationic species that we shall abbreviate as HZ^+ . If we now add small quantities of a base, say, a solution of NaOH, there ensues a chemical reaction that is described by



where Z^\pm is the zwitterion.

An apparent equilibrium constant for this reaction may be written as follows:

$$K_b = \frac{(HZ^+)(OH^-)}{(Z^\pm)} \quad (2)$$

Let us now suppose we have our system in a region of very high pH where the predominant species is the anion, Z^- . Addition of small quantities of an acid, for example, a solution of HCl, will cause the following reaction to occur:



The apparent equilibrium constant associated with this chemical reaction is

$$K_a = \frac{(H^+)(Z^-)}{(Z^\pm)} \quad (4)$$

It is obvious that the total concentration of material at the oil-water interface, $(Z)_t$, is given by the sum of all the species present, i. e.,

$$(Z)_t = (Z^\pm) + (HZ^+) + (Z^-) \quad (5)$$

It should also be obvious that the terms on the right side of Eq. 5 are themselves not independent but are related quantitatively to one another through Eqs. 1 through 4.

It appears at first glance that we are faced with an insurmountable problem: The chemical nature of pitch and its derivatives are extremely ill defined, and no interfacial concentration can be measured experimentally. This problem can be eliminated, fortunately, by expressing all concentrations in terms of (mole) fractions. For example, the fraction of zwitterion, f_\pm , is defined by

$$f_\pm = \frac{(Z^\pm)}{(Z)_t} \quad (6)$$

The following example is given to illustrate how analytical expressions describing the relationships between fraction and pH may be derived (Fig. 2).

$$(Z^\pm) = (Z^\pm) \quad (7)$$

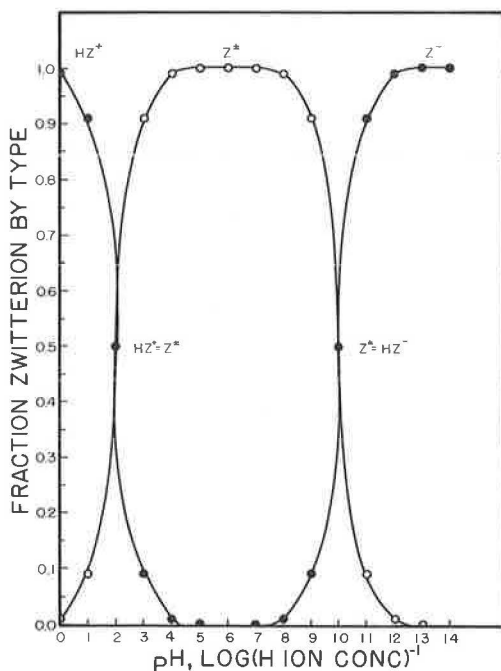


Figure 2. Fractions of cationic (HZ^+), zwitterionic (Z^\pm), and anionic species as functions of pH.

From Eq. 2

$$(\text{HZ}^+) = \frac{K_b (\text{Z}^\pm)}{(\text{OH}^-)} \quad (8)$$

and from Eq. 4

$$(\text{Z}^-) = \frac{K_a (\text{Z}^\pm)}{(\text{H}^+)} \quad (9)$$

Adding Eqs. 7, 8, and 9 and substituting into Eq. 5, we obtain

$$(\text{Z})_t = (\text{Z}^\pm) \left[1 + \frac{K_b}{(\text{OH}^-)} + \frac{K_a}{(\text{H}^+)} \right] \quad (10)$$

There exists another relationship in water and in aqueous solutions that we shall use to eliminate another variable, (OH^-), i. e.,

$$(\text{H}^+) (\text{OH}^-) = K_w \quad (11)$$

Substituting $K_w/(\text{H}^+)$ for (OH^-) in Eq. 10, we find that

$$(\text{Z})_t = (\text{Z}^\pm) \left[1 + \frac{K_b (\text{H}^+)}{K_w} + \frac{K_a}{(\text{H}^+)} \right] \quad (12)$$

Equation 12 is now rearranged to a somewhat different form:

$$\frac{(\text{Z}^\pm)}{(\text{Z})_t} = f_\pm = \frac{(\text{H}^+) K_w}{(\text{H}^+)^2 K_b + (\text{H}^+) K_w + K_a K_w} \quad (13)$$

Likewise, expressions for the cationic (f_+) and anionic (f_-) species may be derived as follows:

$$f_+ = \frac{(\text{H}^+)^2 K_b}{(\text{H}^+)^2 K_b + (\text{H}^+) K_w + K_a K_w} \quad (14)$$

and

$$f_- = \frac{K_a K_w}{(\text{H}^+)^2 K_b + (\text{H}^+) K_w + K_a K_w} \quad (15)$$

To characterize the composition of the interface over the entire pH range requires a knowledge of the values of K_a and K_b . In their original study, Cratin and Dean (2) reasoned as follows:

Aware that the amphoteric asphaltenes are quite similar to the amino acids, we constructed a plot of f^\pm versus pH for glycine. The curve obtained was identical in shape to that in Figure 1. Upon further analysis, it was found that, in the case of glycine the inflection point in the left hand leg occurred when $(\text{Z}^\pm) = (\text{HZ}^+)$, that is, at half-neutralization, so that $\text{pH} = 14 - \text{p}K_b$. On the right hand side, the inflection point corresponded to the condition $(\text{Z}^\pm) = (\text{Z}^-)$ (again at half-neutralization), so that $\text{pH} = \text{p}K_a$. The maximum in the glycine curve occurred at the isoelectric point, i.e., where

$$(H^+) = \sqrt{K_a K_w / K_b}$$

To complete the argument, we reasoned that the interfacial tensions of the asphaltenes are directly related to the fraction of zwitterion present. Thus, f_{\pm} will be a maximum at the charge-neutralization (i.e., isoelectric) point; since the interfacial activity will be a minimum here, the interfacial tension will be at its maximum value. The decrease in f_{\pm} is accompanied by an increase in f_+ or f_- , depending upon pH, and since these materials are more interfacially active than Z^{\pm} , the interfacial tension will accordingly decrease.

It is now possible to use Figure 1 to determine the pH values at which equimolar mixtures of the zwitterion and the charged species co-exist at the interface. From the pH values taken at the two points of inflection K_a and K_b were calculated with the equations: $pK_b = 14 - pH$ (left-hand side) and $pK_a = pH$ (right-hand side). The values of K_a and K_b were found to be: $K_a = 10^{-10}$ and $K_b = 10^{-12}$. A compilation of the fraction of each species as a function of the pH is given in Table 1.

As a consequence of this analysis, there now exists a method to determine whether these species which co-exist at the interface do so independently or do so antagonistically. If they co-exist independently, then the activities of the species will remain constant throughout the pH range over which they are present. Should they exhibit an antagonistic effect, this will be reflected in the inconstancy of their activities.

Successful completion of the argument requires a suitable definition of the interfacial activity, Φ . This variable must be readily calculated from experimental measurements, and its values must have real significance. Cratin and Dean (2) proposed a definition based on the relative lowering of the interfacial activity.

$$\Phi = \frac{\gamma_0 - \gamma_i}{\gamma_0} \quad (16)$$

where γ_0 is the highest interfacial tension exhibited by the system throughout the pH range, and γ_i is the interfacial tension observed under the conditions for which Φ is calculated. This definition is most useful, for not only does it relate to experimentally determinable properties but also it places logical limits on its values. To illustrate this, let us consider a substance (such as a detergent) capable of reducing the interfacial tension to zero. This is equivalent to saying that this substance possesses the maximum degree of activity, i.e., $\Phi = 1$. Conversely, a substance that does not affect the interfacial tension is said to have no degree of activity. Mathematically, $\gamma_i = \gamma_0$, and $\Phi = 0$.

Having chosen a definition for interfacial activity, we must now demonstrate how this will provide information about independent (or not) coexistence. If the various species coexist independently, the total activity will be equal to the sum of the contributions from all species. That is to say,

$$\Phi = \frac{\gamma_0 - \gamma_i}{\gamma_0} = \sum_i \phi_i f_i \quad (17)$$

$$\frac{\gamma_i}{\gamma_0} = 1 - (\phi_{\pm} f_{\pm} + \phi_+ f_+ + \phi_- f_-) \quad (18)$$

The working equation from which a (γ_i/γ_0) versus pH curve is constructed is obtained by substitution of Eqs. 13, 14, and 15 into Eq. 18. The final result is as follows (the reason for plotting the relative interfacial tension in Figure 1 now becomes apparent):

$$\frac{\gamma_i}{\gamma_0} = 1 - \left[\frac{\phi_{\pm} (H^+) K_w + \phi_+ (H^+)^2 K_b + \phi_- - K_a K_w}{(H^+)^2 K_b + (H^+) K_w + K_a K_w} \right] \quad (19)$$

TABLE 1
 f_{\pm} , f_+ , AND f_- AS FUNCTION OF pH

pH	f_{\pm}	f_+	f_-	pH	f_{\pm}	f_+	f_-
0	0.01	0.99	10^{-10}	8	0.99	10^{-6}	0.01
1	0.09	0.91	10^{-9}	9	0.91	10^{-7}	0.09
2	0.5	0.5	10^{-8}	10	0.50	10^{-8}	0.50
3	0.91	0.09	10^{-7}	11	0.09	10^{-10}	0.91
4	0.99	0.01	10^{-6}	12	0.01	10^{-12}	0.99
5	0.99+	10^{-3}	10^{-5}	13	10^{-3}	10^{-14}	0.99+
6	0.99+	10^{-4}	10^{-4}	14	10^{-4}	10^{-16}	0.99+
7	0.99+	10^{-5}	10^{-3}				

Note: $K_a = 10^{-10}$, and $K_b = 10^{-12}$.

Equation 19 contains 3 variables yet to be determined: ϕ_{\pm} , ϕ_+ , and ϕ_- . These can be found in the following manner:

1. At pH=6, nearly all the asphaltenes are in the zwitterionic form. (The fractions of cationic and anionic species are about 10^{-4} .) Hence, as a first approximation, we shall let $f_+ = f_- = \text{zero}$, and $f_{\pm} = 1$. Substituting these values into Eq. 19, we obtain

$$\frac{\gamma_1}{\gamma_0} \rightarrow 1 - \phi_{\pm} \quad (20)$$

Because $\gamma_1 = \gamma_0$ and $\frac{\gamma_1}{\gamma_0} = 1$ at pH = 6, ϕ_{\pm} is found to be zero.

2. At pH = 10, $f_+ = 10^{-8}$, $f_- = f_{\pm} = 0.5$, and $(\gamma_1/\gamma_0) = 0.55$; ϕ_- then is 0.90.

3. At pH = 2, $f_- = 10^{-8}$, $f_+ = f_{\pm} = 0.5$, and $(\gamma_1/\gamma_0) = 0.50$; ϕ_+ is found to be 1.00.

In its final form, Eq. 19 becomes

$$\frac{\gamma_1}{\gamma_0} = 1 - \left[\frac{(H^+)^2 K_b + 0.90 K_a K_w}{(H^+)^2 K_b + (H^+) K_w + K_a K_w} \right] \quad (21)$$

(Recall that these values were obtained by Cratin and Dean's "eyeball" method. Recently, a computer analysis of their data gave the "best values" for K_a and K_b as 9.43×10^{-11} and 9.97×10^{-13} respectively.) The values given in Table 2 were calculated from Eq. 21. A graphical comparison of the theoretical values with experimental data is shown in Figure 3.

Interpretation

The near-perfect agreement between theory and experiment, which extends for 14 orders of magnitude in hydrogen ion concentration, strongly attests to the validity of the model and the assumptions. It is clear that Eq. 21 describes the interfacial behavior of this system very well; and, furthermore, one can state that as-

TABLE 2
 CALCULATED AND EXPERIMENTAL VALUES OF
 γ_1/γ_0 AS FUNCTION OF pH

pH	Calculated γ_1/γ_0	Experimental γ_1/γ_0	pH	Calculated γ_1/γ_0	Experimental γ_1/γ_0
0	0.01	—	8	0.99	1
1	0.09	0.09	9	0.91	0.97
2	0.50	0.50	10	0.55	0.55
3	0.91	0.91	11	0.18	0.18
4	0.99	1	12	0.10	0.12
5	0.99+	1	13	0.10	—
6	0.99+	1	14	0.10	—
7	0.99+	1			

Note: $\phi_{\pm} = 0.00$; $\phi_+ = 1.00$; $\phi_- = 0.90$; $K_a = 10^{-10}$; $K_b = 10^{-12}$; and $\gamma_0 = 21.0 \text{ dynes cm}^{-1}$.

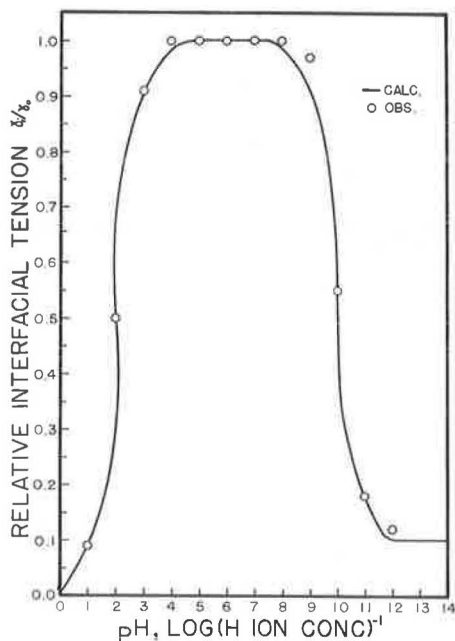


Figure 3. Comparison of experimental and calculated relative interfacial tensions as functions of pH anaerobic).

phalthenes and their derivatives coexist independently at the oil-water interface over the entire pH range. Evidence for any molecular interactions is completely lacking.

Emulsion Stability and pH

The broad maximum shown in Figure 1 occurs in the pH range where water-in-oil emulsion stability is greatest because of the formation of rigid interfacial films. Likewise, it corresponds to the region where the predominant species is the zwitterion. As the pH is changed (raised or lowered), the interfacial tension undergoes a rapid drop to near zero, a value that is necessary for the stabilization of oil-in-water emulsions. These emulsions are stabilized not by rigid films but by "mobile," or surfactant, films (7, 8). In the transition from rigid to surfactant films, the system passes through a phase-inversion point, that is, a region where a water-in-oil emulsion inverts to become an oil-in-water type. Hence, it is at the phase-inversion point that emulsion stability will be at a minimum. Before the phase-inversion point is reached, the great majority of surfactants present at the interface are those tending to stabilize water-in-oil emulsions by the formation of rigid films. Beyond the phase-inversion point, the greater number of surfactant molecules present are those that tend to stabilize oil-in-water emulsions through electrical effects and a low interfacial tension. It is reasonable to assume that regions of instability will occur when approximately equal numbers of surfactants coexist at the oil-water interface—one type tending to stabilize water-in-oil emulsions and the other trying to stabilize the oil-in-water type. These regions of instability correspond precisely to the points of inflection in the γ_i/γ_o versus pH curve. Below the isoelectric point, minimum stability exists when $(HZ^+) = (Z^\pm)$; above, the isoelectric point minimum stability occurs when $(Z^-) = (Z^\pm)$.

A stability-pH profile has recently been proposed by Cratin (9). He defined a stability index, S, for a system containing 2 surfactant species as

$$S = 1 - 2f_1f_2 \quad (22)$$

where f_1 and f_2 are fractions of the respective surfactant species present in the interface.

Table 3 gives a compilation of data calculated by using the fractions (Table 1) and Eq. 22. A plot of S versus pH is shown in Figure 4. An inspection of Figure 4 shows that there are 3 regions of high stability: (a) at low pH values where oil-in-water emulsions are favored because of the presence of positively charged, i.e., cationic, surfactants; (b) at high pH values where oil-in-water emulsions are also favored because the surfactants are nega-

TABLE 3

EMULSION STABILITY INDEX AS FUNCTION OF pH

pH	f_+	f_\pm	f_-	S	pH	f_+	f_\pm	f_-	S
0	0.01	10^{-12}	0.98		8	10^{-6}	0.01	0.98	
1	0.08	10^{-10}	0.84		9	10^{-7}	0.08	0.84	
2	0.25	10^{-9}	0.50		10	10^{-8}	0.25	0.50	
3	0.08	10^{-7}	0.84		11	10^{-11}	0.08	0.84	
4	0.01	10^{-6}	0.98		12	10^{-14}	0.01	0.98	
5	10^{-3}	10^{-5}	1		13	10^{-17}	10^{-3}	1	
6	10^{-4}	10^{-4}	1		14	10^{-20}	10^{-4}	1	
7	10^{-6}	10^{-3}	1						

Note: $K_a = 10^{-10}$, and $K_b = 10^{-12}$.

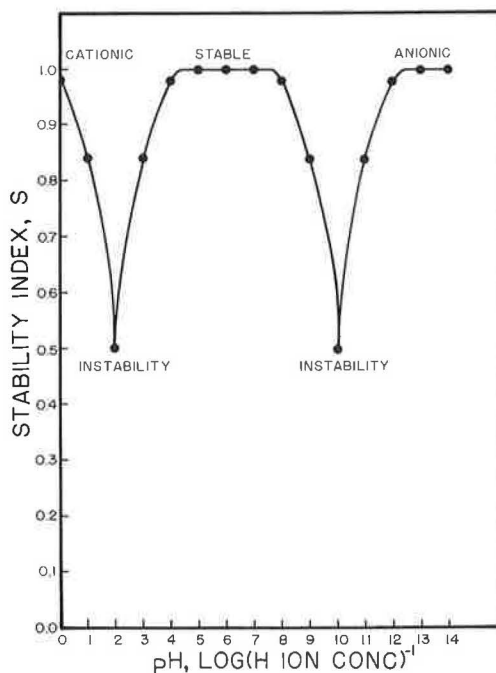


Figure 4. Emulsion stability index as function of pH.

tively charged, i. e., anionic; and (c) at intermediate pH values where water-in-oil emulsions are stable because of the presence of uncharged, i. e., zwitterionic species that offer stability through the formation of rigid films. Likewise, Eq. 22 predicts 2 points of minimum stability: at $\text{pH} = 2$ where $(\text{HZ}^+) = (\text{Z}^+)$, and at $\text{pH} = 10$ where $(\text{Z}^-) = (\text{Z}^\pm)$. These predictions have been confirmed experimentally.

Effect of Oxygen on Asphaltene Behavior

Several interesting observations were made on systems from which air had not been excluded during separation and purification of the asphaltenes. Figure 5 shows the relative interfacial tension as a function of pH under nonanaerobic conditions. The left side of the curve has become truncated to such an extent that it is almost nonexistent, while the right side has changed very little aside from its dropping to near zero at high pH values. The results of a mathematical analysis of these data show that (a) the values of K_a and K_b are, within experimental error, identical to those values of K_a and K_b for the anaerobic asphaltene system; (b) the activity of the anionic species, ϕ_- , rose to 1.00; and (c) the activity of the cationic species, ϕ_+ , dropped to 0.14.

These results can be interpreted in the following manner: The fact that K_a and K_b remained unchanged indicates that the types of chemical groups on the asphaltene "molecule" are probably the same for both classes of asphaltenes. The rise in ϕ_- can be attributed to the increase in the number of acid groups (which, at high pH values, are converted to active soaps) arising from the oxidation of unsaturated chemical bonds in the molecule. The fall in ϕ_+ can be ascribed to the oxidation of some basic groups to nonbasic species. Because the oxidized form cannot react with hydronium ions to become cationic, the overall interfacial activity decreases. A most significant fact is that the method tells the magnitude of the change: 86 percent of the basic groups were destroyed!

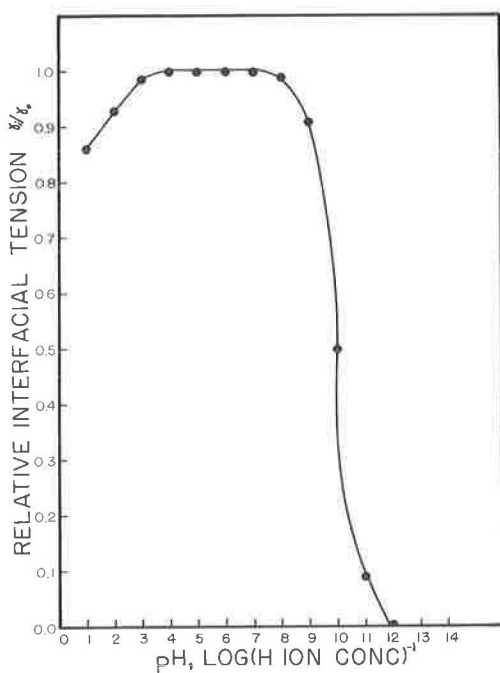


Figure 5. Experimental relative interfacial tension as function of pH (nonanaerobic).

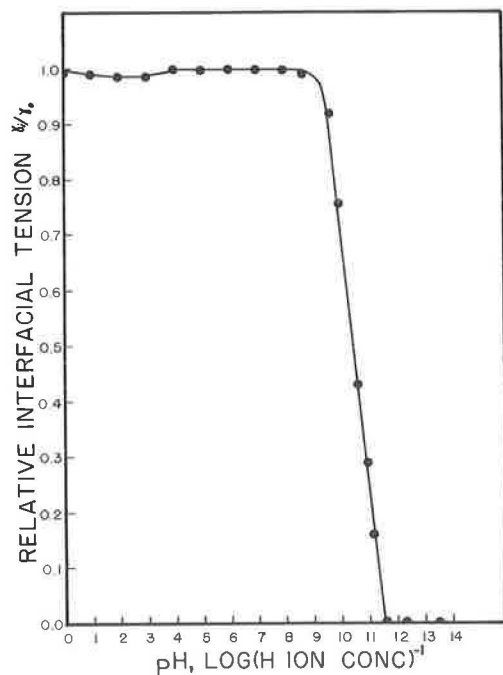


Figure 6. Experimental relative interfacial tension of stearic acid as function of pH.

If this explanation is valid, then a molecule containing only acid (no basic) groups should exhibit large relative interfacial tensions until a region of high pH is reached. To check this, Cratin and Zetlmeisl (10) measured the interfacial tension of a solution of stearic acid as a function of pH. Their findings, as shown in Figure 6, offer unequivocal support for the validity of this explanation.

CONCLUSION

The research described in this paper is but a single example of how this general method, when properly used, can characterize quantitatively any system whose properties are sensitive to pH. Indeed, the phenomenal amount of information that has been gleaned from these experimental data serves to emphasize the utility of this general method and points to its future use to explain the behavior of many such ill-defined systems.

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