Surface pH and Stability of Oil-Water Emulsions Derived from Laurate Solutions

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ABSTRACT

Emulsion stability, electrophoretic mobility, and interfacial tension of chloroform, cyclohexane, and n-hexadecane-potassium laurate solution were determined as a function of acidification by concentrated HCl. The stability of these emulsions were related to the presence or absence of lauric acid at the interface. It was found that a lauric acid-laurate interfacial film was responsible for the enhanced stability in the case of cyclohexane and n-hexadecane emulsions, while no such mixed film existed in the case of chloroform. The interfacial ionization markedly affects the distribution of ions in solution closer to the interface. The concept of surface pH was applied. Differences of up to 2 pH units between bulk and surfaces were found with these systems. Both cyclohexane and hexadecane have major stability peaks which lie at ca. the same surface pH of 5.9 ± 0.2, irrespective of the initial potassium laurate concentration or bulk pH. It is concluded that the stability of these emulsions can be explained when the role played by the interfacial ionization is taken into consideration.

INTRODUCTION

The authors recently investigated the interfacial film composition and surface pH for oil-water interfaces containing laurate soaps as the emulsifier (1). These properties were determined as a function of bulk pH for fixed laurate concentrations by acidifying the system with aqueous HCl. Interfacial tension and electrokinetic potential measurements were used to provide data from which these properties could be determined. An outcome of the study was the hypothesis that emulsion stability of these systems could be influenced or controlled by adjusting the interfacial film composition to attain the optimum stability for a given system.

The objective of the research reported herein was to test this hypothesis with several potassium laurate based emulsions.

Materials

A stock solution of potassium laurate (0.1 M) was prepared by neutralizing 1 mole melted lauric acid, mp 43-45 C, (Eastman Kodak Co., Rochester, N.Y.) with 2 moles KOH. The ionic strength of the diluted laurate solution always was adjusted to 0.01 by KNO_3 (to keep the extension of the electric double layer constant). The oils used were cyclohexane and hexadecane (spectroscopic quality, Matheson, Coleman & Bell, East Rutherford, N.J.) and chloroform (reagent grade, J.J. Baker Chemical Co., Phillipsburg, N.J.).

Titration Curves

Fifty ml dilute (1-5 mM) potassium laurate solution (with excess KOH) was titrated dropwise with HCl (0.2 N) in the presence of 50 ml oil (1). In these titrations and subsequent experiments, the final pH always was brought down by addition of HCl.

Emulsion Stability

Oil in water emulsions was prepared as follows: 20 ml oil was stirred thoroughly (20 min with magnetic stirrer) with 80 ml laurate solution acidified with HCl to a given pH value. After reaching a constant pH for the aqueous phase, the oil was emulsified in a Waring blender at 20 v for 3 min.

The relative stability of the oil in water emulsions was determined by measuring the time (t_o) required for the first visible sign of appearance of the oil phase (2). After the emulsion had been transferred carefully from the blender to a 100 ml graduated stoppered cylinder, the volume (V) of the separated (coalescent) oil phase was measured as a func-

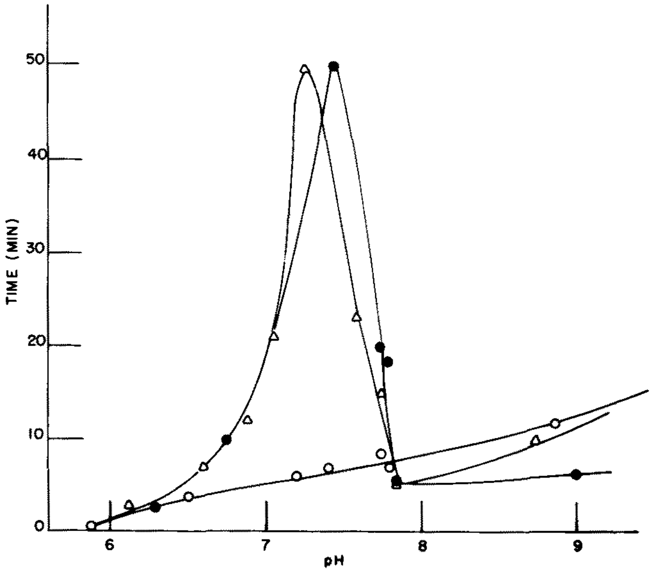

FIG. 1. Relative stability of chloroform (○), n-hexadecane (●), and cyclohexane (△) emulsions in 1 x 10^{-3} M potassium laurate as function of pH.

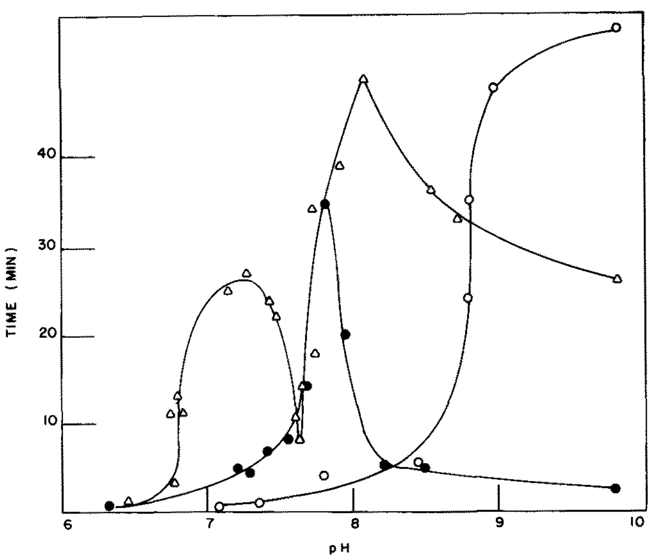

FIG. 2. Relative stability of chloroform (○), n-hexadecane (●), and cyclohexane (△) emulsions in 5 x 10^{-3} M KL as function of pH.

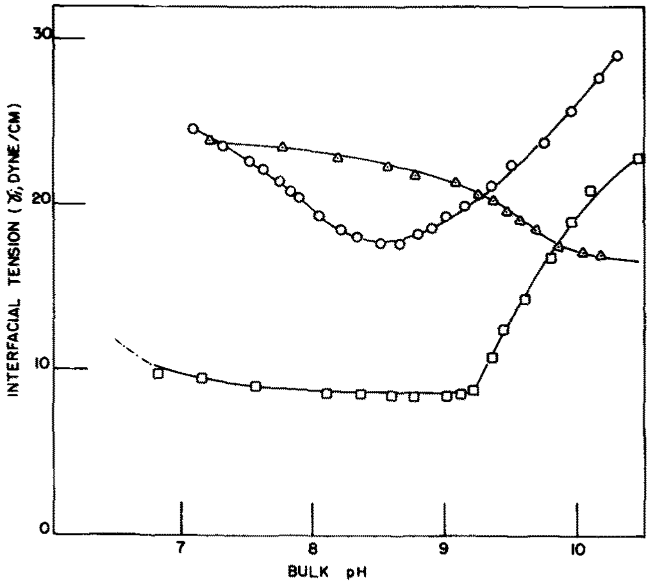

FIG. 3. Interfacial tension vs pH for 5×10^{-3} M KL against chloroform (△), hexadecane (○), and cyclohexane (□).

tion of time. Plots of V vs t (time) were extrapolated to zero volume to obtain t_0. At the end of the stability test, the pH of the aqueous phase was measured.

Electrophoretic Mobility

The mobilities of oil droplets in laurate solutions of different pH values were determined using a cylindrical microelectrophoresis cell (glass-Teflon cell, Zeta Meter, New York, N.Y.). As very dilute emulsions were required for these measurements, the oil was equilibrated with the laurate solution as in the first part of the emulsion stability test, and 0.05 ml of the already equilibrated oil was dispersed ultrasonically (1,3).

Interfacial Tension

A wettable blade method apparatus (Rosano Tensiometer, Biolar Corp., Northgrafton, Mass.) was used to determine air-water and oil-water interfacial tensions.

RESULTS

Emulsion Stability vs pH

Figures 1 and 2 show typical stability curves for 1 and 5 mM potassium laurate solutions as function of degree of acidification (pH). In Figure 1, the stability of $CHCl_3$ emulsion in 1×10^{-3} M KL is low and decreases, apparently due to the decrease in laurate ion concentration as the acidification is increased. On the other hand, the hexadecane and cyclohexane emulsions in 10^{-3} M KL show a surge in stability at pH 7.5 and 7.3, respectively. After that, the stability is significantly low as the pH drops below 7.

Figure 2 shows that with 5×10^{-3} M K laurate, the $CHCl_3$ system become abruptly unstable below pH 9.0. On the other hand, the cyclohexane-KL-water system exhibits two stability peaks around pH 8.1 and 7.2, respectively. From previous titration curves (1), it is estimated that the first peak corresponds to ca. 50% soap acidification while the second, smaller peak is at ca. 90% acidification, i.e. the remaining laurate ion in solution is ca. 5×10^{-4} M. The n-hexadecane-KL-water system also exhibits an enhanced stability around 50% soap acidification (around pH 7.8). No second stability peak could be found for this system at higher acidification levels, as was the case with cyclohexane, where repeated experiments confirmed the two stability peaks.

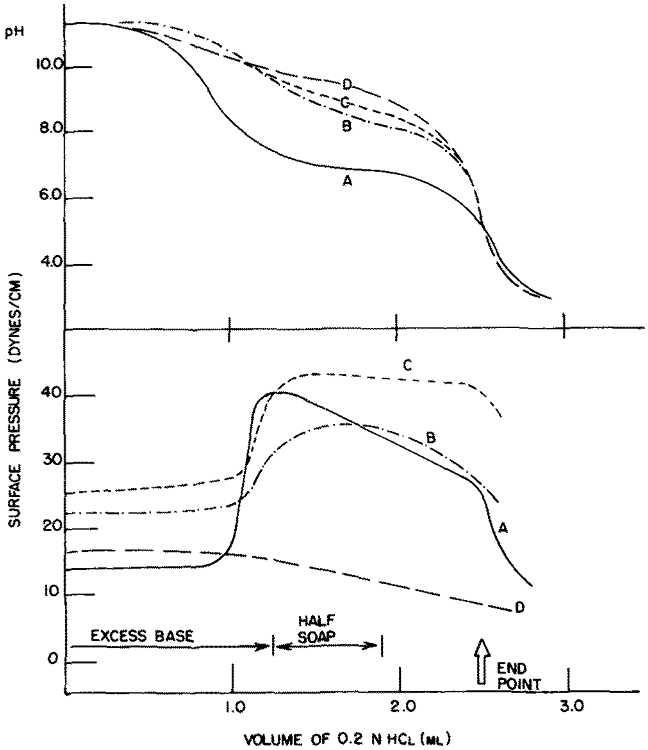

FIG. 4. Titration curve and surface pressure of 5×10^{-3} M KL vs HCl added. A. no oil, B. n-hexadecane, C. cyclohexane, and D. chloroform.

Interfacial Tension and pH

It was found that, for the present oil-laurate-water system, there are generally minima in the interfacial tension (δ_i) at the pH ranges corresponding to maxima in emulsion stability. Figure 3 shows a typical example for the variation of δ_i with pH when using an initial K laurate concentration of 5×10^{-3} M. On the other hand, Figure 4 presents the titration curves of the above systems and the corresponding interfacial surface pressure (π) as function of HCl volume added. ($\pi = [\delta_{i_0} - \delta_i]$ is the difference in interfacial tension between the organic-pure water interface and those values when laurate ions are present at different acidification levels.) The figure shows that the titration curve of this nonmicellar KL solution in the presence of an oil is similar to that of a weak monoprotic acid, such as acetic acid. The presence of an oil-water interface produces an upward shift in the titration curves. The magnitude of the upward shift in pH depends upon the initial laurate ion concentration and the type of oil used (1,4,5), as it reflects the redistribution of lauric acid in the system between the aqueous and oil phases. This will be discussed later. In Figure 4 (curve A), the surface pressure of acidified K soap solutions vs volume of added HCl shows that the surface pressure remains constant (neutralization of excess alkali), then rises (formation of acid soap), and finally drops sharply (conversion of acid soap to lauric acid). This indicates that the acid soap is markedly more surface active than either soap or fatty acid (5). Similar results to the air-water interface were observed in the cases of cyclohexane and n-hexadecane-water interfaces, indicating mixed interfacial layers. However, this behavior is not the case with chloroform; the π curves show a continuous decrease with acidification due to the progressive depletion of laurate ion in the aqueous phase.

Electrokinetic Potentials

The electrokinetic potential (ζ) of droplets of $CHCl_3$, n-hexadecane, and cyclohexane were calculated from the

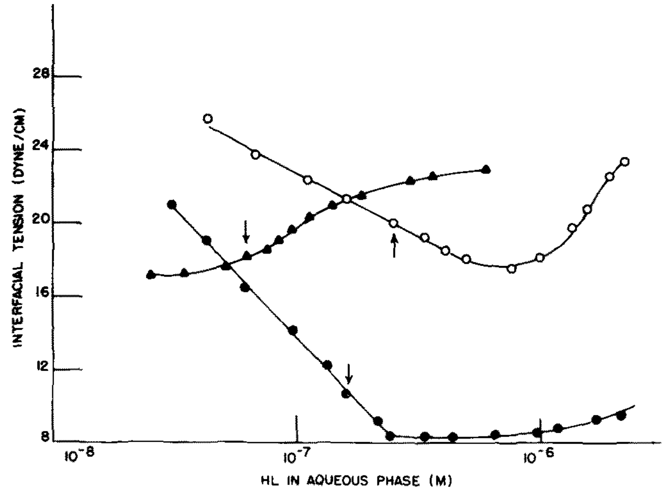

FIG. 5. Interfacial tension vs lauric acid concentration in aqueous phase. Initial laurate = 5×10^{-3} M; chloroform (▲), cyclohexane (●), and hexadecane (○). Arrows locate the laurate concentration of 4.48×10^{-3} M.

determined electrophoretic mobilities at given laurate-lauric acid ratios. The latter was controlled by the initial K laurate concentration and by subsequent acidification by HCl to predetermined values (pH) to correspond with the emulsion stability data. ζ Always was found to be negative and to increase with laurate ion concentration in solution. It is higher for cyclohexane>hexadecane>chloroform for a given laurate concentration. The electrokinetic potential of these oil droplets at several degrees of acidifications was used to calculate hydrogen ion distribution close to the oil-water interface.

DISCUSSION

Role of Lauric Acid in Emulsion Stability

In the titration of these alkaline (pH$\simeq$11) potassium laurate soap solutions with HCl, the concentration of lauric acid in the system, as a whole, increases as the pH is lowered. The formed lauric acid (HL) distributes between the aqueous and oil bulk phases as well as at the interface. The following equilibrium is established in the aqueous phase:

$$\mathrm{HL} \rightleftharpoons \mathrm{H}^+ + \mathrm{L}^- \qquad \mathrm{K} = [\mathrm{H}^+]\,[\mathrm{L}^-]/[\mathrm{HL}], \qquad \text{(I)}$$

where K is the dissociation constant of the fatty acid. The pH of the solution is then given by the general simplified equation:

$$\mathrm{pH} = \mathrm{pK} + \log\,[\mathrm{L}^-] - \log[\mathrm{HL}]. \qquad \text{(II)}$$

From the titration curves and equation II, the lauric acid concentration in the aqueous phase can be calculated at any degree of acidification of the system. Figure 5 shows a typical plot of interfacial tension as function of HL concentration in the aqueous phase when using an initial laurate concentration of 5×10^{-3} M. The arrows on the curves locate the concentration of HL in solution at which the L^- concentration has been reduced, by acidification, from 5 to 4.48×10^{-3} M. It is evident from this graph that, at equal total lauric acid content in the above three systems, there is less lauric acid in the aqueous phase in the case of chloroform compared to the cyclohexane and hexadecane cases. In other words, chloroform extracts HL more effectively than the other oils. A distribution coefficient (D) for lauric acid between the oil and water phases was calculated at that particular point (arrows) and found to be 2.06, 3.27, and 8.21×10^3 for hexadecane, cyclohexane, and chloroform, respectively.

Figure 5 also shows that there is an almost linear decrease of δ_i with the logarithm of HL concentration in the aqueous phase for both hexadecane and cyclohexane. From these linear plots, the adsorption density of lauric acid at the oil-water interface was calculated using the Gibbs adsorption isotherm (6 and J. Th. G. Overbeek, private communication).

The interfacial areas/lauric acid molecule (Å^2) found are shown in Table I. The data in Table I show that, at that particular region in the titration curves (descending δ_i and increasing emulsion stability, the cyclohexane-water interface can support lauric acid molecules more effectively than hexadecane. This condensing effect may be due to the inability of the somewhat spherical cyclohexane molecules to penetrate the interfacial layer effectively as compared with the normal aliphatic chain of hexadecane which is difficult to squeeze out by the interfacial film (7). With chloroform as the oil, it appears that, because of its relative large D value for lauric acid and low adsorptive capacity for laurate ions (1), it cannot support lauric acid at the interface to any significant degree, especially compared to cyclohexane or n-hexanedecane (least D values) or air (Fig. 4, curve D). Inspection of Figure 5 indicates that for the [HL] to be appreciable in the aqueous phase ($>10^{-7}$ M) and to achieve increased adsorption in the presence of chloroform, a higher degree of acidification has to be reached. However, at such a point, the aqueous $[\mathrm{L}^-]$ is reduced significantly. The effect, consequently, is the laurate adsorption density at the interface also is reduced, thus reducing the ability to form a mixed film, since laurate is essential for supporting HL at the interface.

Stability and Surface pH

The above measurements and calculations show that a mixed surface film of laurate-lauric acid does occur in the pH region of maximum emulsion stability. A consideration of the ionic distribution in the aqueous side adjacent to the oil-water boundary would be useful in understanding this behavior. Due to the negative charge at these interface (due mainly to L^- adsorption), the hydrogen ion concentration close to the interface should be higher than that in the bulk far from the interface. Assuming a Boltzmann hydrogen ion distribution between the bulk and the charged interface, Danielli (8-10) and Hartley and Roe (11) have related the bulk and surface pH ($\mathrm{pH_B}$ and $\mathrm{pH_S}$, respectively) by the following relation:

$$\mathrm{pH_B} - \mathrm{pH_S} = \mathrm{nF}\psi/2.303\mathrm{RT}. \qquad \text{(III)}$$

ψ Is the electrochemical potential different across the interface, and nF/RT have their usual meaning. A Boltzmann distribution implies a diffuse electrical double layer; in this

TABLE I

Interfacial Areas/Lauric Acid (HL) Molecule

Initial laurate concentration (M)	Area/HL molecule (Å^2) at:	
	Hexadecane/water	Cyclohexane/water
5×10^{-3}	135	67
2×10^{-3}	152	96
1×10^{-3}	215	150

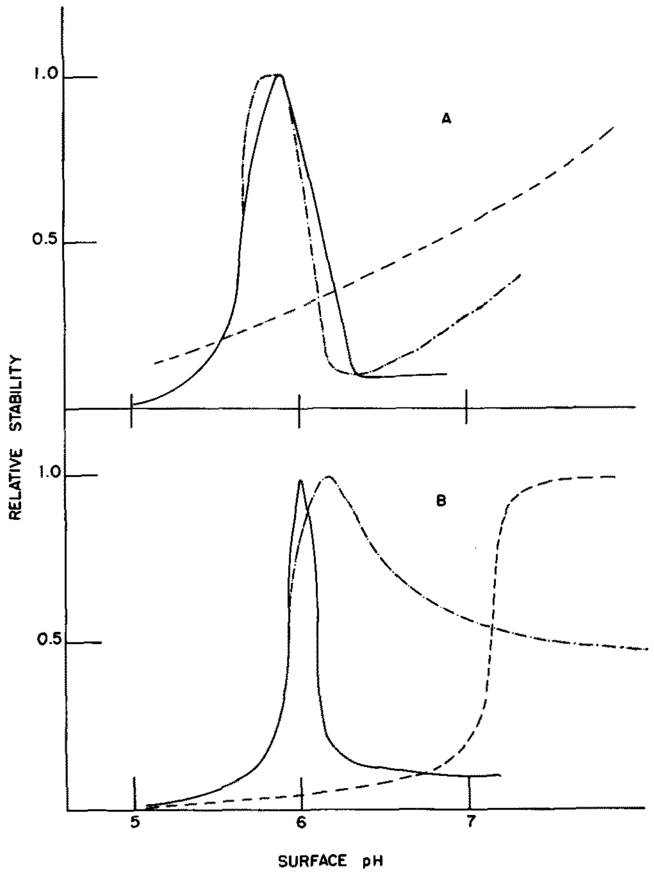

FIG. 6. Emulsion stability vs calculated surface pH. (——) hexadecane, (—) chloroform, and (-----) cyclohexane. A = 1 x 10^{-3} M KL; B = 5 x 10^{-3} M KL.

case, Hartley and Roe have shown that the electrokinetic potential ζ may be substituted for ψ. Using this approximation for a 1:1 electrolyte, equation III may be written:

$$pH_S = pH_B + F\zeta/2.303RT$$

or

$$pH_S = pH_B - \zeta/59 \qquad \text{(IV)}$$

at 25 C for ζ values in millivolts. Utilizing the data from Figures 1 and 2, the emulsions' relative stabilities were replotted in Figure 6 as a function of the surface pH, where the surface pH was calculated using the electrokinetic data and equation IV. It is evident from Figure 6 that both cyclohexane and hexadecane have major stability peaks which lie at ca. the same surface pH of 5.9 ± 0.2, regardless of the initial K laurate concentration (whether 1 or 5 mM). This result leads to the conclusion that a *particular interfacial structure between lauric acid and laurate ion must exist at the hexadecane-water and cyclohexane-water interfaces* at the point of maximum emulsion stability, but this is not the case at the chloroform-water interfaces. It should be mentioned that a 1:1 bulk mixture of L^-/HL, termed acid soap, is produced when a K laurate solution is acidified and has been reported to have a pKa of 6.2 (4,12,13). Furthermore, it is probable that a continuous series of compositions of HL/L^- does occur at the interface as a function of pH (composition is determined by bulk pH and [L^-] solution). Figure 6 suggests that when the emulsion stability reaches an optimum, an interfacial composition close to 1:1 HL/L^- is achieved.

The variation of the calculated so called surface pH as function of acidification is shown in Figure 7. Acidification (abscissa) is represented by the ratio of total L^-/total HL in the system (sum of HL in all phases). It clearly is demonstrated that, regardless of the initial K laurate concentration, an acidification around 50% is required to achieve a surface pH of ca. 6.2 for the cyclohexane and hexadecane systems only, but not for the chloroform. For the chloroform system to be at a surface pH of 6.2, an acidification of more than 90% has to be reached. At this region, the laurate concentration is too low to support HL, hence a compact interfacial layer which would enhance stability cannot form.

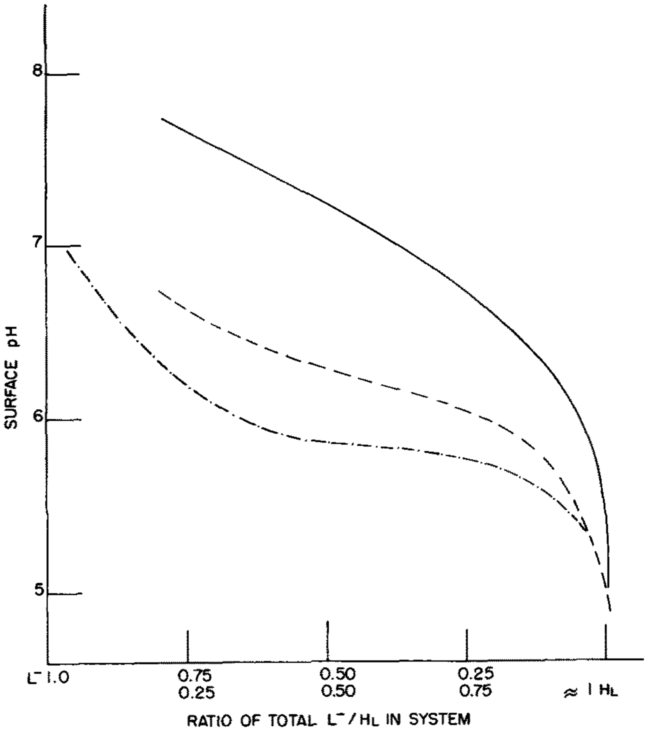

FIG. 7. Calculated surface pH vs degree of acidification of potassium laurate solutions in presence of chloroform (———), cyclohexane (—), and hexadecane (-·····).

The data in Table I also show a significant difference between the cyclohexane and hexadecane interfaces in the ability to abstract lauric acid from solution, especially at high initial K laurate concentrations (5 x 10^{-3} M). This may explain the appearance of two peaks in the stability-pH curve for cyclohexane (Fig. 2) and the absence of a second peak for hexadecane. For both oils, the laurate ion adsorption is almost the same (106Å^2/laurate ion over the concentration range 1-5 x 10^{-3} M). The first stability peak for the cyclohexane system (pH$\simeq$8.1) may be an acid soap-soap stabilized emulsion, while the second one (pH$\simeq$7.2) may be acid-acid soap stabilized (the latter peak is not shown in Fig. 6). The in-between peak will correspond to a surface inversion.

Given the approximation that the surface pH is based upon a Boltzmann distribution of ions and that the electrokinetic potential is of the same order of magnitude as the electrochemical potential, the authors feel that the concept of surface pH explains the enhanced emulsion stability. Our study primarily was designed to serve as a model to explain the importance of interfacial ionization on the emulsion stability of oils.

Our conclusion allows one to understand the effect of trace amounts of free fatty acid in vegetable oils-water emulsions. In the systems discussed herein, the maximum amount of free fatty acid used is ≈40 mg, or 0.2%, if all of it is present in the oil phase (20 ml oil/80 ml aqueous solution). The present data also indicate that as little as 0.04% free fatty acid is sufficient to enhance stability of hexadecane and cyclohexane emulsions if the right pH is reached. This also was found to be true when using safflower oil with 10^{-3} M K laurate. An enhancement in emulsion stability can be achieved by the simple adjustment of pH.

Also, the concept of surface pH would explain the reported shift in the functioning pH of immobilized enzymes and emulsion stability with proteins. Where different functional groups or surface-active molecules are involved, the surface pH may be up to 3 pH units higher or lower than the bulk pH, depending upon the magnitude of the interfacial electrical potential and whether it is positive or negative, respectively (14-18).

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