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Transient Foaminess, Aggregate Formation, and Wetting Behavior in Water-Phenol Mixtures

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Liquid mixtures of phenol and water exhibit foaminess only for one-liquid phase states rich in water. Foam stability shows a sharp maximum around $x^* \sim 7-8\%$ (weight) phenol. We confirmed that the surface tension drops rapidly with addition of phenol and that after the same x^* is reached it remains practically constant. Conductivity measurements indicate a change in behavior at roughly the same composition. In the two-liquid region the contact angle of the two liquids with air, or with their own vapor, never vanishes, indicating partial wetting at all temperatures. However, two different regimes can be distinguished and they are separated by the temperature T^* when the water-rich liquid is of composition x^* . We discuss the thermodynamic behavior of the water-rich/air interface that is consistent with these manifestations of surface activity.

Introduction

We have undertaken the study of the aqueous/air interface in phenol-water mixtures through determinations of transient foam stability, surface tension, three-phase contact angle, and electric conductivity. These measurements provide a picture of interfacial thermodynamics in this system that we discuss in terms of interrelations between bulk and interfacial phase behavior.

The lifetime of the network of liquid films that form a foam is largely determined by the adsorption or segregation that takes place at surfaces of liquid mixtures. For mixtures, in contrast to pure substances, the contraction of liquid films is made difficult by the work required to transfer the segregated components from the surface to the bulk solution. If this amount of work counterbalances the energy gained by contraction of surfaces the liquid film is thermodynamically stabilized.^{1,2} On the other hand, the mechanical stability against film thinning is dependent on the net force on the film surfaces as a function of thickness. It has been shown³ that, in general, this force at (the liquid-vapor) thermodynamic equilibrium is always attractive. Hence, most dilute solutions of surface-active components can only produce transient foams^{3,4} made of thick films. The films thin gradually and when they reach a critical value disappear. Therefore, to maintain a foam it is necessary to keep the solution under agitation. However, solutions of a few suitable amphipathic surfactants like soaps, detergents, and proteins (i.e., with a molecular structure with well-defined hydrophilic and lipophilic solvent interactions) can develop persistent foams that after drainage are formed by polyhedral cells of very thin walls. A soap film, if unperturbed, can be thinned until it suddenly transforms into a black film of less than 200 Å that is basically constituted of two tight monomolecular lamellae of surfactant.^{5,6}

The differences between these two types of mixtures become manifest in their bulk properties. A binary mixture with solute molecules that have no clearly defined amphipathy, like, for example, methanol in *n*-heptane, often have phase diagrams exhibiting partial miscibility of liquids (free of association structures) and three-phase states (a vapor, V, and two liquids, L_1 and L_2) terminating at upper critical end points.⁷ On the contrary, a

mixture containing a conventional amphiphile, such as soap and water, proceeds through a series of micellar and liquid-crystalline phases with increasing soap concentration.⁸ Further, there is evidence that the thermodynamics of interfaces also differ for the two kinds of mixtures. Interfacial transitions for the first type become associated to immiscibility, these are the so-called wetting transitions,^{9,10} whereas for the second type where there is saturation of one monolayer of soap they appear related to micellization.⁸

Interfacial Thermodynamics, Wetting, and Micellization

When a liquid-vapor two-phase state (L_1V) is driven toward three-phase equilibrium (L_1L_2V) an interesting transformation occurs to the structure of the $L_1|V$ interface, but only provided the three-phase point exhibits perfect wetting (i.e., when the contact angle of the three possible interfaces vanishes indicating that the $L_1|V$ interface is intruded by a macroscopic film of liquid L_2).^{9,10} Close to such a triple point, the equilibrium $L_1|V$ interface contains a microscopic film resembling an L_2 metastable phase. When the three-phase point is approached by increasing the concentration of component 2, in which L_2 is rich, this will be preferentially admitted at the interface without alteration of its microscopic character. This regime continues until saturation of the interfacial region occurs when the only alternative to change in global composition is the appearance of phase L_2 in bulk. The thickness of the L_2 -like film increases logarithmically^{9,10} as perfect wetting is approached indicating a second-order interfacial transition. Additional information on this process is obtained by observation of the behavior of the second derivatives of the interfacial free energy F .⁴ In the neighborhood of such triple points the interface develops rigidly toward admission of component 2, and F shows a pronounced curvature in the direction of the parameter that quantifies this admission. At the same time laxity is generated with respect to interfacial region widening, which is manifest as a slight curvature of F in the direction of the parameter that represents the width of this region. At the triple point one of these curvatures diverges while the other vanishes, signalling the instability of the interface.⁴ A clear connection has been suggested⁴ between transient foaming and the occurrence of wetting interfacial transitions in partially miscible liquids, where the behavior of F described above corresponds to the enhancement of foam stability as immiscibility is approached, followed by complete defoaming action once the second liquid appears in the bulk.¹

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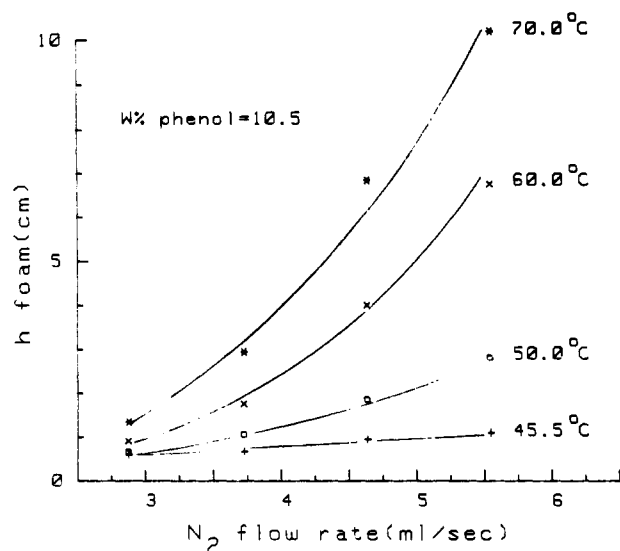


Figure 1. Dependence of foam column height h on gas flow rate G .

In the case of a binary mixture where one component is an amphiphile at low concentration this will place itself almost exclusively at the L_1/V interface, finding there a preferential orientation that energetically favors the formation of a monolayer.⁸ In a manner analogous to that described above, the increment of solute concentration eventually saturates the interfacial region forcing its instability. Under these circumstances the interface, of microscopic character, requires an alternative that would let it occupy volume, only now the appearance of a third phase, partially miscible in the former two, is not favored. The aggregation of the amphiphiles into colloidal associations dispersed into the solution is the prevailing alternative.

Clearly, the distinction between the two types of mixture behavior just outlined is only a simplifying scheme, for there are mixtures that incorporate elements of both cases. For instance, a phase diagram may combine aggregate formation at low concentrations followed by an immiscibility region for further surfactant additions. It is of interest to investigate both foam stability and wetting properties for such a system, for then the suggested relationship between liquid-film stability and interfacial thermodynamics can be given added perspective. With this purpose we chose to examine the phenol-water system. This is a readily available mixture with a thoroughly studied¹¹ phase-separation diagram and with a reported surface tension vs. composition behavior suggestive of aggregate formation.¹¹ Surface tension diminishes rapidly when phenol is added to pure water to a value of 0.55 times that of water at a concentration of 7% (weight) phenol. After this, the surface tension remains practically constant. It seems, therefore, that the water/air interface becomes quickly saturated by phenol forming a compact adsorbed monolayer and that a probable appearance of colloidal association shields the interface from thickening in phenol concentration. Preliminary tests showed appreciable foaminess for the water-rich liquids, as well as facility to suspend material of the denser phenol-rich liquid at the water-rich/air interface in the two-liquid region.

Experimental Section

Materials. Phenol of 99% purity supplied by J. T. Baker Co. was further purified through successive crystallizations until thermal analysis produced a single melting peak at $T = 41 \pm 1$ °C. The solutions were prepared with twice distilled water and the measured average conductivity was $1.5 \mu\text{mho cm}^{-1}$. The critical solubility point (at Mexico City's altitude) was located at $x = 34.5 \text{ wt } \%$ and $T = 66.5 \pm 0.5$ °C.¹¹

Foam Stability Measurements. The foam meter employed was of the type designed by Ross and Nishioka.¹ It consisted of a glass

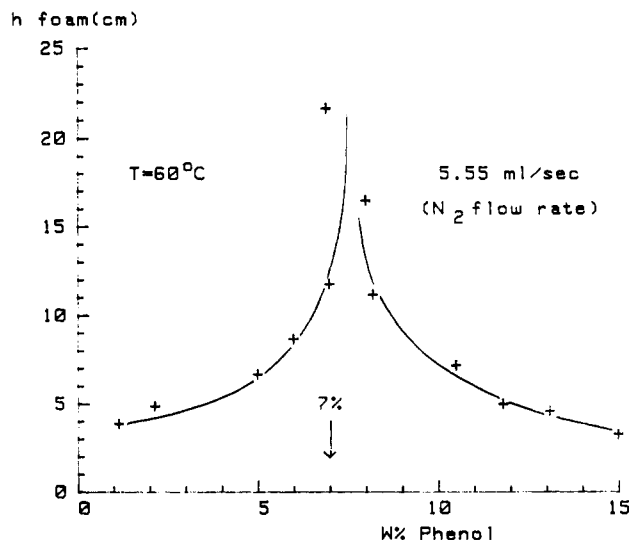


Figure 2. Isothermal variation of foam column height with composition for water-rich mixtures at $T = 60$ °C.

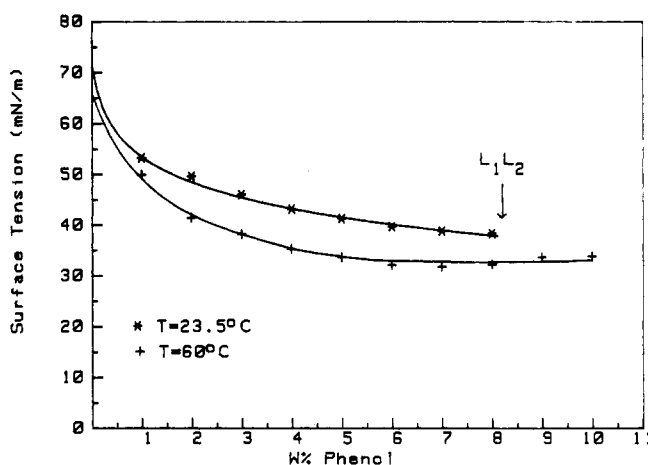


Figure 3. Surface tension of the water-rich/air interface in the one-liquid region. The arrow indicates the position of the immiscibility curve at 23.5 °C. That for 60 °C occurs at 14% phenol.

cylinder with a temperature control jacket. The dimensions are 3 cm interior radius and 35 cm height. Nitrogen was used as the foaming gas and its flow rate G was controlled with a calibrated rotameter. The liquid level and the foam column height h were measured with a cathetometer. All runs had the same initial volume of solution.

The measure of foam stability originally proposed by Bikerman² and employed by Ross and Nishioka¹ implies a linear relationship between foam volume and gas flow rate. Our experience indicated deviations from linearity over extended G values and poorer reproducibility due to variations in the bubble size distribution.¹² For these reasons we present our results at constant flow rate. Figure 1 shows the variation of h vs. G for a mixture of $x \sim 10.5\%$ phenol. Foam behavior was studied between 30 and 60 °C, and appreciable foaminess was found only in the one-liquid, water-rich region of the phase diagram. A pronounced maximum in h , as shown in Figure 2 was detected at all of these temperatures around $x^* = 7\text{--}8\%$ phenol.

Surface Tension. The tension of the water-rich/air interface in the one-liquid region was determined with a Du Noüy (Cenco 70535) tensiometer with temperature control and the measured values were corrected as in ref 13. In Figure 3 we show our results for $T = 23.5$ and 60 °C. These data were fitted by the monolayer isotherm equation of Szyszkowski,¹⁴ and this in turn indicated that

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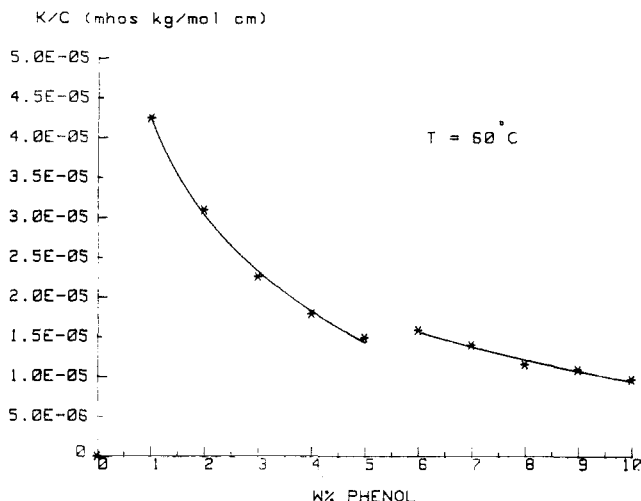


Figure 4. Molal conductivity of the bulk water-rich solutions at 60 °C.

the saturation surface concentration C_s is attained very rapidly with addition of phenol to pure water. At $x^* = 7$ wt % phenol we obtain $0.99C_s$ for 23.5 °C and $0.97C_s$ for 60 °C.

Conductivity Measurements. The electric conductivity of the bulk solutions were measured with a conductivity bridge (Leeds & Northrup 4959) under temperature control. In Figure 4 we show the molal conductivity for $T = 60 \pm 0.5$ °C.

Angle of Contact. The contact angle between the two liquids and air (or with their own vapor) was determined through the photographic registration of droplets, or lenticules, of phenol-rich liquid suspended at the water-rich/air interface. Mixtures with global critical composition were placed in a glass cylindrical cell of 2 cm diameter and 8 cm height with a built-in temperature control jacket and a capillary valve (Gilmont M7200) on the upper end. The latter was employed to extract air from the cell for some of the runs. The cell was set in a vibration-free optical bench with a horizontal photographic camera (Leitz, $f = 8$ cm). The images were registered on 10×12.5 cm² plates and read with a bidimensional microscope (W.G. PYE & Co. Ltd. 6147) featuring 10^{-4} -cm precision. The determination of contact angles needed the reading of at least three points on the linear sections of the liquid-liquid and the phenol-rich/air interface in the vicinity of their intersection. The cell temperature was controlled with a thermal bath (Lauda K-2/R) with a precision of ± 0.01 °C. Before each photographic registration the mixture was periodically agitated at a fixed temperature for 30 min and then allowed to phase separate completely. In the vicinity of the critical solution point the time necessary for phase separation was longer than 90 min. Measurements were made at 5 °C intervals from 20 to 65 °C. In Figure 5 we show our results for the air-evacuated mixtures.

Discussion

From the results of measurements shown in Figures 2–4, we distinguish two different regimes for the one-liquid water-rich region of the phase diagram located below the critical solubility temperature $T_c = 66.5$ °C. The two regimes are separated by an almost vertical line in the T - x diagram situated around $x^* = 7$ -8 wt % phenol.

The first regime begins with pure water and corresponds to the build up of a monolayer of phenol at the water/air interface. The development of the dilute adsorbed layer progressively decreases the surface tension and increases foam stability. The conductivity (molal conductivity) of the bulk solution also increases (decreases) with phenol concentration, showing two different regimes. The situation in the foam meter is probably the following: the surfaces of newly formed bubbles, while inside the solution, capture available phenol molecules as they rise toward the surface of the liquid column. Those bubbles that approximate the current

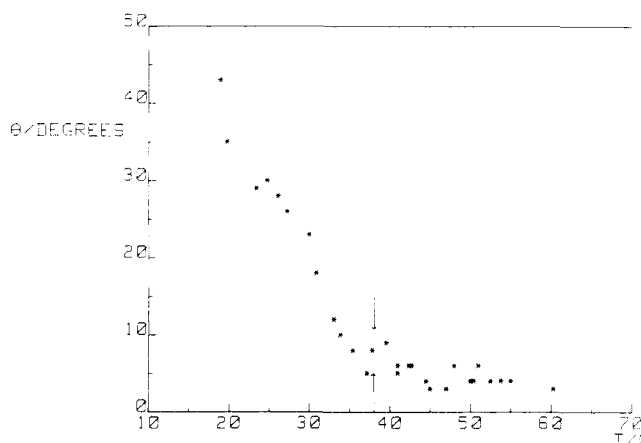


Figure 5. Variation of the angle of three-phase contact with temperature for air-evacuated mixtures. The arrows indicate the temperature when the water-rich liquid is 7–8% phenol.

equilibrium interfacial concentration produce the more stable liquid films, and as bulk concentration increases this process becomes more efficient. The thick liquid films that constitute the foam column above the liquid solution also see their stability augmented as phenol becomes more tightly packed at their surfaces.

The second regime, located between the x^* boundary and the immiscibility curve, is characterized by the constancy of the surface tension and bulk conductivity, also, a complete reversal in the behavior of foam stability is observed, with foaminess decreasing with increasing phenol concentration. The constancy of the surface tension seems to indicate that the adsorbed layer has become compact and that it maintains a fixed composition independent of the bulk concentration. The assumption that some form of phenol aggregation occurs at x^* explains not only the behavior of the surface tension and conductivity, but also the gradual abatement of foam stability. Foam films become less stable since now reductions of their surface area are not diffculted by the unfavorable transfer of segregated phenol to the bulk liquid. Adsorbed layers can be readily accommodated through colloidal association.

These two regimes of the water-rich/air interface also manifest in the temperature dependence of the angle of contact θ in the two-liquid region. In Figure 5 we observe that θ decreases rapidly from values around $\theta = 43^\circ$ when $T = 20$ °C to about 8 – 7° at $T^* \approx 38$ °C, and thereafter θ decreases slowly to zero at T_c . The highest tension at the L_1L_2V triple points is that of the water-rich/air interface and it would be here where perfect wetting may appear.^{9,10} An examination¹¹ of the composition attained in the water-rich liquid at T^* on the immiscibility curve indicated that it is again x^* , and therefore the slowly varying regime of θ for $T^* \leq T \leq T_c$ is attributable to a buffered state of the interface through aggregation. The clear transition observed at T^* in Figure 5 suggests that the measurement of the angle of contact θ is a useful method to investigate aggregate formation of micellization in systems where there is partial miscibility.

The observed foam conduct with composition and temperature is consistent with the finding that no partial-to-perfect wetting transition takes place at the water-rich/air interface and that all three-phase states up to T_c present finite contact angles. (The same behavior was obtained in the air-evacuated samples.) When there is perfect wetting, maximum foam stability should occur⁴ at the immiscibility curve followed by a sudden collapse of the foam column when the second liquid separates out.^{1,4} In a model calculation¹⁰ of the wetting properties for simple (van der Waals) binary fluid mixtures it is found that the occurrence of partial wetting at all temperatures is an unlikely event restricted to mixtures with special symmetries or to large values of the heat of mixing. The most common behavior in mixtures of nonpolar, spherical molecules corresponds to a first-order partial-to-perfect wetting transition with perfect-wetting states adjacent to the critical end point. Therefore, in practice, partial wetting at all

temperatures must indicate competition with other interfacial events likely to take place only in mixtures of nonspherical, polar, or amphiphathic molecules. Colloidal association and micellization are events of this type and the resulting buffered water-rich interface cannot be driven through the second-order transition, by means of which a phenol-rich film thickness as the two-liquid region is drawn near. The orientational arrangement that takes place at the interface only favors the formation of a monolayer and not that of a macroscopic wetting film. On the other hand, foams of phenol-water solutions are not persistent, an implication that their liquid films cannot be drained to a stable structure of

two close adsorbed layers of phenol. This behavior is consistent with a bulk phase diagram that does not exhibit lamellar lyotropic liquid crystal phases. Careful observation of a foam column may develop into one of the simplest experimental methods to detect interfacial singularities associated to wetting, aggregation, micellization, and other related phenomena.

Acknowledgment. We are grateful to C. Varea for valuable discussions. Financial support by Consejo Nacional de Ciencia y Tecnología de México is also acknowledged.

Registry No. Phenol, 108-95-2.

Photoassisted Oxygenation of Olefins: An Exchanged Zeolite as a Heterogeneous Photosensitizer

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$\text{Ru}(\text{bpy})_3^{2+}$ exchanged into zeolite Y acts as an effective, heterogeneous singlet oxygen sensitizer. The photogenerated singlet oxygen freely diffuses to solution where it reacts with normal selectivity. The photocatalyst has high catalytic turnover, and its high stability permits its reuse.

Introduction

Heterogeneous photosensitizers have a number of practical advantages over soluble analogues. For example, sensitizer molecules held in a defined environment are site-isolated, decreasing self-quenching and side reactions. In addition, supported sensitizers can sometimes function in solvents where the dye itself is inactive and can be easily separated from the reaction mixture either by filtration or sedimentation.¹

These heterogeneous photosensitizers are usually prepared in one of three ways: by covalent attachment to cross-linked polymers or other solid supports, by adsorptive immobilization on a solid surface, or by incorporation into a polymeric film. We report here the use of a heterogeneous photosensitizer prepared in an alternate way, by inclusion within a zeolitic cavity, and describe its activity in generating singlet oxygen.

Exchanged zeolites²⁻⁸ have recently been investigated as heterogeneous photocatalysts. As an extension of our interest in heterogeneous photoreactions,⁹ we have prepared zeolites exchanged with an organometallic complex, $\text{Ru}(\text{bpy})_3^{2+}$, tris(2,2'-bipyridine)ruthenium(II), **1**, and have studied its use as a photosensitizer.

The inclusion of **1** in a zeolite was first reported by Lunsford in 1980.⁷ The complex was synthesized in the zeolite cavity by allowing 2,2'-bipyridine to react with $\text{Ru}(\text{NH}_3)_6^{3+}$ -exchanged zeolite Y. The spectroscopic properties of the intrazeolitic com-

plexes were similar to those exhibited by **1** complexes in aqueous solution. Faulkner and co-workers studied **1** in zeolite X prepared by impregnation.⁸ They reported that the complex stays intact and can undergo one-electron transfer with *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD), 10-phenylphenothiazine (10-PP), and tetrabromo-*o*-benzoquinone (TBBQ), maintaining solution redox properties in the zeolite cavity. The size of 10-PP prevents it from entering the zeolite pores, accounting for the different redox chemistry when compared with TMPD. The bimodal decay of the excited state in luminescence quenching studies was attributed to the complex occupying two different sites in the zeolite. These studies were directed toward the characterization of the zeolite, leaving potential photocatalytic applications unexplored.

In solution, excited **1** produces singlet oxygen,¹⁰ which can then undergo an "ene" reaction with olefins to form allylic hydroperoxides.¹¹

Experimental Section

Zeolite Preparation. In accord with published procedures,¹² 35-60-mesh LZ-Y52 zeolite powder (Union Carbide) was stirred at room temperature for 24 h in a 7 mM solution of **1** buffered by tris(hydroxymethyl)aminomethane (pH 8.2). The exchange solution was filtered with a fine glass frit, and the filtrate was analyzed by absorption spectrophotometry. The concentration difference between the filtrate and starting solution was attributed to the exchange of the complex for Na^+ in the zeolite. The loading levels were also obtained by spectrophotometric analysis of the exchanged zeolites dissolved in a solution of 1 M citric and hydrofluoric acid. Filtration with a fine glass frit yielded a light yellow, exchanged zeolite that was washed with water and

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