Electric Fields across Water-Nitrobenzene Interfaces

Abstract. *Surface-active ions in water-nitrobenzene systems accumulate at the interface in electric fields. Two separate mechanisms can be distinguished. One is similar to the classical electrocapillary adsorption and the other is operative when there is appreciable transference across the interface. The magnitude of the interfacial barrier to transport determines which mechanism operates.*

When an electric field is formed across a liquid-liquid interface one can expect a change in the interfacial concentration of the ions present by either of two mechanisms. An example of the better known mechanism is the behavior of mercury in contact with an aqueous electrolyte solution. An electric field causes an adsorption of cations or anions depending on the direction of the field (or rather, the state of charge of the mercury surface). Because there is negligible transference through the interface, the interface is not discharged and ions are adsorbed by electrostatic interaction. This results in a decrease in the interfacial tension that depends on the magnitude of the potential at the mercury surface. This phenomenon is called electrocapillary absorption and the mechanism has been investigated quite thoroughly (*1*).

The second mechanism that gives rise to changes (increases as well as decreases) in interfacial concentration is operative when there is transference through the interface. This mechanism was studied (*2*) with simple salts in a water-phenol system. The change in concentration occurs primarily at the interface but, owing to diffusion, extends into both phases as time passes.

The water-nitrobenzene system studied here (*3*) is one that offers a liquid-liquid interface of two fairly high dielectric materials in which one can dissolve a variety of solutes. The transport of ions across this interface has been studied (*4*) and recently Guastalla (*5*) has shown that an electric field across the interface in the presence of a charged surface-active agent produces changes in the interfacial tension.

We have used both the techniques of Guastalla and of electrocapillary adsorption in an attempt to characterize the water-nitrobenzene interface. From our evidence each of the two mechanisms, dependent upon solubility relations, can lead to changes in the interfacial concentration of ions. If the ion is soluble in the aqueous phase only, it behaves apparently as in electrocapillary adsorption. If it is soluble in both phases, it exhibits the type of behavior described by Nernst and discussed above. The possibility of both mechanisms operating simultaneously under certain conditions is not ruled out.

The interfacial tension of water-nitrobenzene (both distilled) was 25.80 dyne/cm at 25°C. Solubilities and partition coefficients between the two solvents were determined by conductivity for a number of surface-active ions. Two classes of substances were tried: (i) amino acids, soluble in the aqueous phase only and (ii) cationic surface-active agents (for example, cetyltrimethylammonium bromide, CTAB), soluble in both phases. The interfacial tensions in the presence and absence of electric fields were determined by the drop-weight method in the case of amino acids and by the dipping-plate method in the case of CTAB.

Figure 1 shows the values of interfacial tension for glycine and for glutamic acid in water as a function of the voltage applied across the interface. The curves show a decrease in interfacial tension associated with electric fields in both directions, indicating an adsorption of both cations and anions. When the *p*H of the experiment is close to the isoelectric point (6.06 for glycine, 3.08 for glutamic acid) one expects the adsorption of amino acid at positive and negative values of the electric field. (A positive value means that nitrobenzene is positive with respect to the water.) If the experiment is conducted at a *p*H above the isoelectric point one loses part of the anionic portion of the electrocapillary curve since the surface-active ion, the amino acid, is now primarily in the cationic form. These and other experiments show that this system is similar to a classical electrocapillary system.

Figure 2 shows the behavior of the surface (interfacial) pressure with time for CTAB solutions when a constant current is made to pass through the interface. The change in the surface tension caused by a surface-active material is the surface pressure of the material and the interfacial concentration is simply related to the surface pressure in the concentration range studied. Unlike electrocapillary adsorption the interfacial tension varies with time and one can get increases and decreases in interfacial concentration indicating desorption as well as adsorption. The magnitude of the change of concentration depends on the magnitude of the current and the data indicate an initial rapid change followed by a slower, more sustained change with time. Similar results can be obtained for a constant electric field across the interface if one plots the interfacial tension as a function of total amount of charge transferred.

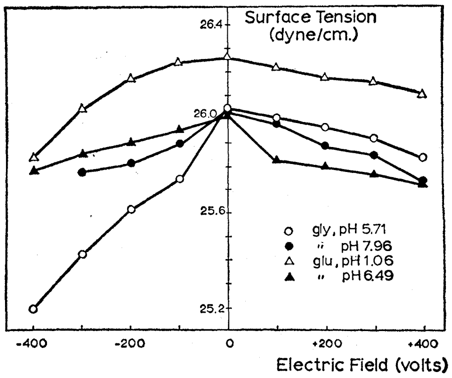

Fig. 1. The interfacial tension as a function of the electric field imposed across the water-nitrobenzene interface when $10^{-3}M$ amino acid is dissolved in the water at various *p*H's. The open symbols are for glycine and for glutamic acid at *p*H's below their isoelectric points. The shaded symbols are of the same amino acids above their isoelectric points.

The mechanisms that have been discussed probably apply to all interfaces where one has charged substances present. The work of Hurd *et al.* (*6*) on the interface of aqueous solution and

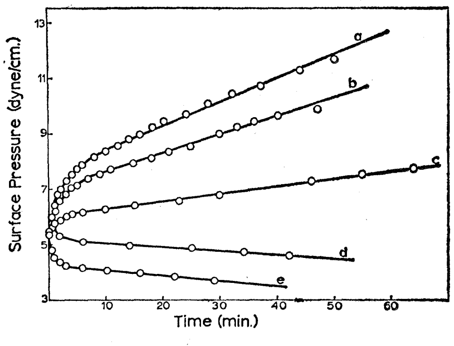

Fig. 2. The variation in CTAB surface pressure with time at a water-nitrobenzene interface when different currents are passed through the interface. The values of the current in microamperes are: *a*, 150; *b*, 106; *c*, 52; *d*, —93; and *e*, —208. The CTAB is initially $0.96 \times 10^{-4}M$ in water and $1.55 \times 10^{-4}M$ in nitrobenzene, this being the equilibrium partition at 25°C.

air, where changes in the surface tension occur with changes in electric field, appears to be an example of a generalized electrocapillary type system. The second ion accumulation mechanism may be more applicable to the situation in natural membranes where appreciable transference does occur under the influence of an electric field. This mechanism may cause transient changes in the concentration of ions at the inside or outside membrane surface when one imposes electric fields across natural membranes to induce an impulse (for example, action potential in nerves). This has been suggested (*7*) in an initial attempt to formulate relevant physical mechanisms for excitable membranes.

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Cavity Formation in Thin Films of Viscous Liquids

Abstract. *High-speed photography was utilized to observe the dynamic growth behavior of a cavity in a viscous liquid. From these observations it has been shown that a relatively elementary analytical approach will reproduce the general cavity growth characteristics.*

The analysis of devices utilizing thin viscous films is often complicated by the occurrence of flow separation. Because of the resulting "free boundary" of the liquid-gas interface, it becomes necessary to furnish additional boundary conditions over those required for the more common problem with fixed boundaries. To gain an insight into the circumstances contributing to the formation of these cavities, a combined experimental and analytical program was initiated. This report is a summary of the results of this program, which were presented at the 1962 General Motors Research Laboratories symposium, Cavitation in Real Liquids (*1*).

In the experimental program cavities were formed by pulling apart two parallel surfaces between which was entrained a viscous liquid. From observations of the growth patterns of these cavities, it was possible to compare the analytical results based upon thin-film approximations with the actual cavity growth.

One of the two surfaces used in the cavity growth process was an optical flat 2 inches (about 5 cm) in diameter. Its mounting fixture was constrained by two flexure plates so as to be always parallel to a ground steel surface. The initial separation between the surfaces was of the order of 0.0005 cm. A motor-driven cam forced the surfaces apart at a rate which was sufficient to initiate the growth of a cavity while the area surrounding the optical flat was continuously flooded with a viscous liquid. The initiation, growth, and collapse of the cavities occurred in about 0.5 second, at which time the separation width was approximately 0.089 cm. A continuous record of the plate separation width was obtained through the use of a preloaded cantilever beam transducer element which bore upon a steel pin which passed through the optical flat holder and made contact with the steel surface. A high-speed camera was used to record the cavity formation at 7000 frames per second, the pictures being taken through the optical flat.

Since films of the order of 0.0025 cm are extremely difficult to observe, even with dyes added, it was necessary to use a material which would fluoresce under ultraviolet light. The liquid used was a petroleum base fluid which has a viscosity of 15 centistokes at 26.7°C, a surface tension of 34.9 dyne/cm at 23.3°C, and a specific gravity of 1.008 at 15.6°C.

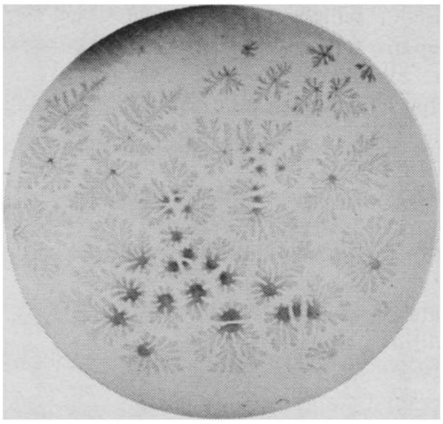

Fig. 1. The growth of cavities in a thin film of a viscous liquid between two parallel plates. The fracturing cavity front assumes a dynamic fern-like structure with increasing time.

Because of the symmetry of the system, as the surfaces are separated one might expect to find a lowering of the pressure within the film until a cavity was formed at the center of the disk, when the cavity would expand with polar symmetry until the time it collapsed. This did not prove to be correct. There was no single cavity formation; instead, there were many small circular voids which occurred at random over the surface of the optical flat. This phenomenon can be attributed to the effects of surface defects acting as nucleation sites and of the presence of dissolved gases in the fluid. Various areas within the film are capable of sustaining different levels of reduced pressure before a cavity forms because of local conditions existing in the film. Consequently, as the pressure is lowered, this local threshold value for cavity formation may occur at several locations in the film before the effect of the aggregate cavities precludes the formation of new voids. The continued growth of each circular void was marked by a fracturing of the cavity front and by the extension of radial runners, as shown in Fig. 1. From these radial growth patterns there appeared many subordinate finger-like appendages growing, in general, at an angle inclined to the growth direction of the radial arterial extensions. The interactions of these extremely unstable

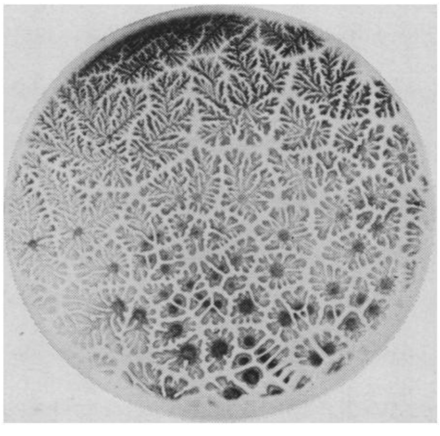

Fig. 2. The coalescence of many separate cavities into one circular cavity. The residual oil appears in the form of filaments throughout the cavity area.