

Interfacial Mass Transfer vs. Formulation in Multiple Phase Anionic Surfactant-Oil-Water Systems

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ABSTRACT: Mass transfer through a liquid membrane was studied in a macroscopic setup that allowed an estimate of the resistance to interface crossing. It was found that the interfacial transfer was associated with the phase behavior and physicochemical formulation of the surfactant-oil-water system. The resistance to interfacial mass transfer closely followed the variation of interfacial tension, i.e., it was minimal at the optimal formulation of the so-called Winsor III phase behavior systems.

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Mass transfer through a liquid membrane has been known for decades (1) since Li's pioneering works (2). Among the various liquid membrane techniques, the emulsion liquid membrane (ELM) method has been studied (3,4) and applied to the separation of hydrocarbons (5), in biochemistry (6) and to metals separations (7,8). Transfer through an ELM may ultimately be facilitated by the reaction between the solute and a reagent in the membrane phase, generally known as type I, or the presence of a carrier in the membrane phase, generally known as type II (9), to counterbalance the effects of low solute solubility (10).

The transfer depends upon various factors such as the concentration gradient across the membrane, geometrical characteristics of the system, and various physicochemical properties such as solubility, bulk diffusion coefficients and resistance to interfacial crossing. The effects of most of these factors have been studied with the exception of the resistance to interfacial crossing, which is analyzed in this report as a function of physicochemical formulation.

EXPERIMENTAL PROCEDURES

In all cases, the transfer involves a sequence of steps in which a solute or tracer goes from the bulk of initial phase *i* to the bulk of final phase *f*, after having passed across the

liquid membrane phase. In what follows, an oil liquid membrane *O* is inserted in between two water phases, *W_i* and *W_f*, as illustrated in Scheme 1 (left). At time zero, water phase *W_i* contains the tracer at a certain concentration *C_i(0)*, whereas *W_f* does not contain any tracer. Tracer concentrations in both water phases, *C_i* and *C_f*, are monitored vs. time, in order to estimate the transfer rate.

In practice, phases *i* and *f* are located at the bottom of two glass beakers kept in a constant-temperature bath, while phase *O* is common to the top part of both beakers. Scheme 1 (right) indicates the main features of the experimental apparatus. Each water phase is kept homogeneous by gentle magnetic stirring, typically at 40–50 rpm, while the oil phase is recirculated from the top of one beaker to the top of the other by a peristaltic pump. The oil level is maintained by a gravity return. Stirring and recirculation are kept to a low energy level so that no emulsification takes place. However, these are believed to be sufficient to ensure good mixing of each of the three phases so that all of them may be considered to be homogeneous at any time. Experimental evidence shows that a 50% change in the stirring and pump settings does not significantly alter the transfer results. Consequently, molecular diffusion through the bulk would not play any role, and the transfer resistance would probably be limited to a thin layer near the interface crossings, as indicated by the solid arrows in Scheme 1.

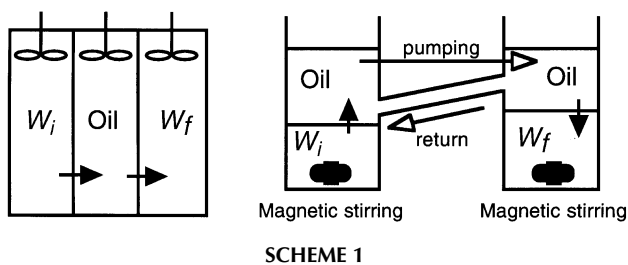
Both water phases exhibit the same physicochemical formulation, as far as surfactant and water phase nature are concerned. Of course, they do not exhibit the same tracer concentration. The selected tracer is phenol because of its solubility in both water and oil phases, and because its concentration is easy to measure by ultraviolet absorbance at 270 nm. The oil phase is reagent grade *n*-heptane. Temperature is kept constant by means of a water bath at $28 \pm 0.5^\circ\text{C}$.

Composition of the water phases is selected after typical phase behavior studies of surfactant-oil-water (SOW) systems, which is normally investigated by changing the aqueous phase salinity (11).

Since dodecyl sulfate is extremely hydrophilic, the optimal formulation for three-phase behavior is found at a very high salinity, unless a lipophilic alcohol such as pen-

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tanol is added (12). However, such an alcohol is known to influence the physicochemical formulation, which is an additional complication that can be avoided by adding *sec*-butanol instead. This latter alcohol is known to have essentially no formulation shift effect (13,14), its role being only to increase disorder and to "melt" any liquid crystal that could form, particularly near optimal formulation. Hence, 2 vol% *sec*-butanol is added to all systems.

In order to reduce the salinity to be dealt with, a mixture of hexadecyl sulfate (25%) and dodecyl sulfate (75%) sulfate sodium salts is chosen instead of pure dodecyl sulfate. Although a higher content of hexadecyl sulfate would lead to a lower salinity, it would also raise the Kraftt point above ambient temperature and eventually produce precipitation.

The critical micelle concentration (CMC) in pure water of the 25:75 surfactant mixture is estimated by conductrimetric and surface tension measurements at 0.18 wt%. It is found to be insensitive to the presence of 5000 ppm of phenol. On the other hand the effect of 2% *sec*-butanol is barely noticeable, raising it to 0.20 wt%. This indicates that the change in salinity is, by far, the main effect on the physicochemical formulation, as well as on the CMC. In fact, adding 4 wt% sodium chloride in water lowers the CMC below 0.02 wt%.

Formulation scan. It has been well known during the past 20 yr that the interfacial tension may attain an ultralow minimum at the so-called optimum formulation where three-phase behavior is also attained (11,13,15). The adjective "optimum" comes from the fact that this is the best formulation to recover petroleum globules that are trapped by capillary forces in the reservoir pores after waterflooding (16).

Such an optimal formulation is sought by carrying out a unidimensional scan, that is, a sequence of SOW systems in which one of the formulation variables is continuously changed while all others are kept constant (11,13,14). As in

most ionic surfactant systems, aqueous phase salinity is chosen as the formulation variable. Several SOW systems are prepared with identical composition and formulation except the aqueous phase salinity, and they are allowed to equilibrate for 24 h at constant temperature ($24 \pm 1^\circ\text{C}$). They are then poured into the apparatus, splitting the water phase between the two beakers. The respective volumes of W_i , O and W_f are 85, 220 and 135 mL. The higher W_f volume establishes the difference in level that drives the gravity return of the oil between beakers. Just before the experiment is started a small amount of phenol (0.425 g) is added to water phase W_i . Oil phase is gently poured on top of W_f phase. When the oil phase is distributed on top of both beakers, the peristaltic pump is started in order to initiate the experiment. Small water phase samples are withdrawn from time to time, and their phenol concentrations are measured with a UV spectrophotometer set at 270 nm.

The first line of Table 1 presents a typical result for the phase behavior with concentration slightly above the CMC of the surfactant mixture, so that three-phase behavior is visually detected at optimal formulation of a salinity scan (expressed as wt% NaCl in aqueous phase). The phase behavior is denoted by Winsor symbols I, II, or III (17) which are used by most researchers (11,13,15). In Winsor I two-phase systems, most of the surfactant partitions into the aqueous phase, and the affinity of the interfacial surfactant-alcohol mixture is for the aqueous phase. Similarly, in Winsor II systems, most of the surfactant partitions into the oil phase, and the affinity of the interfacial surfactants alcohol mixture is for the oil phase. In both cases, the surfactant-rich phase is readily detected by laser light scattering, even at a very low surfactant concentration, just slightly above the CMC. In a Winsor III system, three-phase behavior is exhibited; most of the surfactant partitions into the microemulsion middle phase, the surfactant affinities for the aqueous and oil phases are equal, and the interfacial tension undergoes a very low minimum. At or near the CMC, the microemulsion middle phase vanishes, and the Winsor III three-phase behavior turns into a two-phase low-tension system (11,15).

Three-phase behavior takes place in the 12–14 wt% NaCl range, and optimal formulation is taken at 13 wt% NaCl. The presence of a microemulsion is associated with possible micelle-like association structures that may act as carriers through the interface. To avoid this undesirable eventuality, the surfactant concentration should be reduced to a low value. However, studies on surfactant mix-

TABLE 1
Phase Behavior of Surfactant-Oil-Water System as a Function of Salinity^a

Concentration of alkyl sulfate (wt%)	Salinity (wt% NaCl in aqueous phase)									
	0	4	8	10	12	13	14	15	17	19
0.1	I	I	I	I	III	III	III	II	II	II
0.06	I	I	I	I	I	?	?	II	II	II

^aPhase behavior is denoted by Winsor symbols I, II, or III (17), as used by many researchers (11,13,15).