

The length of the alkyl chain of surfactants, alkanols, and alkanes has been found to strikingly influence the properties and structure of the interface of two contacting phases (1-13). Spreading pressure measurements show that the packing of surface active molecules is altered in mixtures with different alkyl chain length causing an increase of 0.05 Å in the intermolecular distance between the head groups and influencing the interfacial tension and many other properties of the system (1, 2). In addition, other measurements (12-14) indicate that molecular packing plays an important role in many cases of "closed" association structures, such as micelles and microemulsions.

Further, for microemulsions there exists a pure component oil chain length which solubilizes more water for a specific surfactant/alcohol pair than any other (4, 5). This was interpreted as a structural "chain length compatibility" effect (4). The concept was that maximum solubilization of water in the microemulsion would occur due to maximum cohesive interaction between paraffinic chains when $l_a + l_o = l_s$, where the chain lengths are l_a for the alcohol, l_o for the oil, and l_s for the surfactant. The matching of the chains would leave no dangling terminal groups whose thermal motion would decrease the order of the interfacial structure as was found in the interfacial area experiments.

However, the idea of a molecular structural "compatibility" being important in phase behavior is likely to be inconsistent with other recent measurements. Georges *et al.* (15) have obtained a phase diagram and solubilization capacity similar to that for dodecane when the "oil" is methylene chloride, which has no chain at all. Salager *et al.* (16) and Iskanderani (17) show that binary oil mixtures can behave the same as a pure-component oil for flow through porous media, interfacial tension, solubilization, and optimal salinity of three-phase microemulsion systems. Also, Lianos *et al.* (18) show that oil mixtures can give similar properties to pure hydrocarbons for oil-in-water microemulsions. It is apparent that chain matching on a molecular scale could not occur in these cases.

Further, the condition of maximum "cohesive interaction" between the paraffinic chains at the compatible chain length might imply less of the fluidity that is essential for the interfacial film of a microemulsion phase (19, 20). A thermal disruptive effect resulting from a chain length "incompatibility" between the surfactant and cosurfactant would be expected to enhance fluidity, rather than diminish it.

All of these results indicate that molecular structure effects may not be required for establishing a particular phase

behavior. Here we probe more into the nature of the chain length effect in water-in-oil microemulsions with measurements on systems having both pure-component and binary mixtures of normal alkanes. Mixtures of aliphatic hydrocarbons are nearly ideal and the observed symmetries in the small excess Gibbs energies and enthalpies lead to the "principle of congruence" (21), a simple concept for characterizing alkane solution properties. One statement of the principle is that a single pure *n*-alkane of "equivalent alkane carbon number" (EACN) can be found whose properties are the same as those of a mixture. The basic relation is

$$\text{EACN} = \sum_i x_i C_i,$$

where C_i is the carbon number of alkane i , and x_i is the corresponding mole fraction. In addition to bulk properties (21), Cash *et al.* (22) have shown that the interfacial tension of binary hydrocarbon mixtures follows an EACN rule. This idea suggests a set of experiments to test the structural argument of "chain length compatibility." Solubilization of a binary oil microemulsion will differ from that of a microemulsion with single oil if molecular packing is important. In particular, no optimum EACN should be found for mixtures. However, if the results turn out to be the same in all respects, only the bulk oleic phase properties determine the effect of the oil constitution on the phase behavior. The measurements referred to above indicate that the latter could be the case.

We have performed solubilization limit measurements for water-in-oil microemulsions formed by sodium stearate and normal pentanol as a function of alkyl chain length of normal alkanes from C_6 to C_{16} to see if there is an optimum in mixed oil systems. Sodium stearate (LOT-CC-6581) was obtained from ICN Pharmaceuticals, Inc. The samples were prepared by mixing together 10 ml of oil, 8 ml of pentanol, and 1 g of sodium stearate, and then titrating with water at ambient conditions. The solubilization limit of water was the appearance of turbidity which could be reproduced to better than 0.1 ml. All binary oil mixtures were prepared on a molar basis to give the desired EACN; their titration sample preparation was the same as for pure *n*-alkanes except that the oil was 10 ml of the binary mixture. The second column of Table I shows that maximum solubilization in pure oil does occur around C_{12} to C_{13} . Structural "chain length compatibility" would suggest C_{13} as the maximum for this system. However, the third column of Table I shows that the solubilization capacities of the binary oil mixtures are essentially the same as those of the single oils at the EACN chain length.

TABLE I
Water Solubilization Limits for Sodium Stearate/*n*-Pentanol Microemulsions

Carbon number ^a	Pure <i>n</i> -alkane solubilization ^a	Binary mixture solubilization ^b	Components in binary mixtures
6	5.6	—	—
8	6.6	6.6	C ₆ + C ₁₂
10	7.1	7.2	C ₈ + C ₁₆
		7.2	C ₆ + C ₁₂
12	9.1	9.0	C ₈ + C ₁₆
13	8.7	8.7	C ₁₀ + C ₁₆
14	8.4	8.1	C ₈ + C ₁₆
16	7.2	—	—

^a Actual carbon number for pure oils, EACN for binary mixtures.

^b ml H₂O/(10 ml oil + 8 ml *n*-pentanol + 1 g sodium stearate) ± 0.1 ml.

This is true even for mixtures of widely disparate chain lengths such as C₈ + C₁₆.

Thus, the phase behavior of water-in-oil microemulsions is independent of the molecular structure of the oil and therefore also of the interfacial film. Rather, the bulk phase properties, such as the surfactant and alcohol activity in the oil, probably determine the influence of oil constitution on solubilization and other phase behavior of microemulsions.

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