

Equation 3 has been used to describe the behavior of alkanes solubilizing into aqueous micellar solutions of various surfactant types (3,5-8). The term  $(b/a)$  is found to be proportional to the equilibrium solubilization capacity of the micelle for the homologous series of *n*-alkanes (7). Comparisons among oils of differing architecture (5) indicated that the constant of proportionality between the equilibrium and kinetic values of the solubilization capacity was different, possibly reflecting differences in the oil packing in the micelle. A further development upon the packing requirements of the micelle-solubilize aggregate has been made (8,11) in the consideration of solubilization from binary oil mixtures. It was shown (11) that, within the restriction of no preference in the solubilization of the oil components (i.e., the composition of the solubilize mixture remaining the same as the bulk contacting oil phase), relationships of the following form should apply.

$$b_1 = x_1 \{ (x_1 b_1^0 + x_2 b_2^0) - x_1 x_2 P \} \quad [4a]$$

$$b_2 = x_2 \{ (x_1 b_1^0 + x_2 b_2^0) - x_1 x_2 P \} \quad [4b]$$

where  $b_i^0$  are the solubilization capacities of the pure oils and the  $x_i$  represents the oil mole fractions in the binary mixtures. The value of the factor  $P$  can vary between zero and  $(1 + b_1^0/b_2^0)$ , the former value representing ideal mixing of the solubilize in the micelle interior. Comparison of data determined from kinetic experiments with values determined at equilibrium show agreement in the value of  $P$  required to fit the data in some cases (8), whereas, in others, different values are needed in each case. The solubilization of oil from dodecane-tetradecane mixtures into micelles of the non-ionic surfactant *n*-dodecylhexaoxyethylene glycol ether,  $C_{12}EO_6$ , (12) shows good agreement (Fig. 4a) with a  $P$  value of 1.3 (i.e., very close to ideal mixing). In contrast, solubilization from similar mixtures into a micellar zwitterionic surfactant, *n*-dodecyltrimethylammonium propane sulfonate, shows (Fig. 4b) that, although the equilibrium data require  $P = 0$ , the kinetic data is fitted only if the maximum possible value of  $P$  is used. This discrepancy may be a result of micelle shape changes in the first stages of the solubilization process that are not considered in the derivation of Eq. 4. A further manifestation of micellar shape changes that occurs in the initial stages of solubilization is the nonlinear temperature dependencies observed for the rates in the region of the phase-inversion temperature of some nonionic surfactants (5,8).

One consequence of the proposed mechanism is that the rate is essentially independent of stirring in the system, unlike the passive