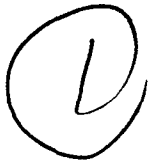


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**SURFACTANT ADSORPTION BY SUB-MILLIMETER SIZE BUBBLES:
QUANTIFICATION AND MODELLING**

Final Technical Report for ONR Contract No. N00014-91-J-1771

Prepared by

Richard A. Skop
Division of Applied Marine Physics
Rosenstiel School of Marine and Atmospheric Science
University of Miami, Miami, FL

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complexity in ascertaining adsorption rates.

Our objective was to quantify these factors and to develop and verify a model of the bubble scavenging process based on experimental results obtained by our group under a previous ONR Contract (N00014-89-J-1354).

Technical Accomplishments

We have completed the reduction of our existing experimental data on bubble scavenging rates of surface-active organic materials in distilled water, artificial seawater and "cleaned" artificial seawater (Skop et al. 1993). The adsorption equation has been integrated based on approximations appropriate to the flow fields encountered in the experiments. This integrated equation serves as the foundation for analyzing the experimental data to obtain functional dependencies of adsorption rates on parameters of the flow and bubble fields.

The principal finding of our research (Skop et al., 1994) is that the rate of scavenging by a rising bubble of diameter d (cm) in a turbulent flow field is given by the equation

$$\frac{dn}{dt} = w\pi d^2 \frac{0.0499 e^{-71f}}{Sc^{2/3} Re^{0.29}} \frac{k_a}{k_{as}} \left(1 - \frac{n}{n_{eq}}\right) C \quad (1)$$

Here, n (gm) is the quantity of surfactant scavenged by the bubble, n_{eq} is the equilibrium value of n based on the balance between adsorption and desorption, C (gm/cm³) is the bulk concentration of

the surfactant, and Sc is the Schmidt number for the surfactant. The bubble Reynolds number based on the rise velocity w (cm/s) is designated by Re and the rise velocity itself is given by

$$w = 4(1 - 0.75e^{-71f})w_c \quad (2)$$

where w_c is the rise velocity for a single "dirty" bubble. In equations (1) and (2), the term e^{-71f} accounts for the observed effects of the local void fraction f on the scavenging process and on the bubble rise velocity. The influence of adsorption kinetics on the scavenging process is contained in the term k_a/k_{aS} in equation (1). Here, k_a is the dimensionless adsorption coefficient for the material being scavenged and k_{aS} is the dimensionless adsorption coefficient for a reference material, in our case stearic acid.

Equation (1) synthesizes the results of experiments previously conducted by our group on microbubble scavenging. The experiments covered a range of bubble Reynolds numbers (approximately 10 to 150) and bubble void fractions (approximately 0.08% to 1.3%) and examined the scavenging of four low molecular weight, hydrophobic lipids (oleic acid, stearic acid, triolein and cholesterol). Our results revealed substantial differences in the susceptibility of these materials to being scavenged. In Table 1, the values of k_a/k_{aS} obtained from bubbling tests and from mixing tests are summarized. In the latter tests (Brown et al., 1992), an initial

TABLE 1. Values for k_a/k_{as}

Material	Mean Value from Bubbling Tests	Mean Value from Mixing Tests
Oleic Acid	3.469	5.397
Stearic Acid	1.000	1.000
Triolein	0.474	0.741
Cholesterol	0.116	0.050

amount of material was injected into our test tank and mixed with a magnetic stirring bar. The transfer of this material to the water surface is governed by the adsorption equation in the form

$$\frac{dn}{dt} = wk_a A C \quad (3)$$

where n is now the total quantity of surfactant at the water surface, A is the area of the water surface, and w is a characteristic velocity near the water surface. The characteristic velocity is unknown. However, for identical mixing processes, we have

$$\frac{dn}{dt} / \frac{dn_s}{dt} = \frac{k_a}{k_{as}} \quad (4)$$

From Table 1, we see that the values of k_a/k_{as} obtained from both

bubbling and mixing tests are similar, as they should be. We also see that, in order of susceptibility to being scavenged, we have oleic acid (an unsaturated fatty acid with mw = 282.5), stearic acid (a saturated fatty acid with mw = 284.5), triolein (a triglyceride with mw = 885.4), and cholesterol (a sterol with mw = 386.6).

Significance of Accomplishments

Our model for predicting surfactant scavenging by bubbles in a bubble cloud provides excellent quantitative agreement with previous measurements. The model, based on turbulent diffusion and kinematic adsorption processes, explains the increase in surfactant adsorption rates with increasing bubble Reynolds number and the decrease in surfactant adsorption rates with increasing bubble plume void fraction. The model identifies the ratio $k_a/k_{a,s}$ of dimensionless adsorption coefficients as the dominant molecular property affecting adsorption rates. Methodologies for measuring $k_a/k_{a,s}$ have been developed.

However, several terms in the model are understood only very approximately and a host of questions remain to be answered before a complete physical description of microbubble scavenging can be formulated. Among these questions are the reasons for the strong dependence of the scavenging rate on bubble void fraction and the possible influences of a multi-component surfactant background on the scavenging process.

Publications

The following publications resulted, in whole or in part, from the research conducted under ONR Contract No. N00014-91-J-1771.

- J.W. Brown, R.A. Skop, J. Viechnicki and R-S. Tseng (1992). "Transport of Surface-Active Organic Materials from Seawater to the Air-Water Interface by an Ascending Current Field," Fluid Dynamics Research, V. 9, pp. 97-105.
- C. Peng (1992). "Influence of Surface Tension on the Jet Formed by a Surface Disturbance." MS Thesis, University of Miami, Miami, FL.
- R.A. Skop, R-S. Tseng and J.W. Brown (1993). "Effects of Salinity and Surface Tension on Microbubble-Mediated Sea-to-Air Transfer of Surfactants," Journal of Geophysical Research, V. 98, pp. 8489-8494.
- R.A. Skop, J.T. Viechnicki and J.W. Brown (1994). "A Model for Microbubble Scavenging of Surface-Active Lipid Molecules from Seawater," Journal of Geophysical Research, in press.

Participants

The following investigators participated in the research conducted under ONR Contract No. N00014-91-J-1771.

- Richard A. Skop, Principal Investigator, Professor, Division of Applied Marine Physics.
- John W. Brown, Research Associate Professor, Division of Applied Marine Physics.
- Ruo-Shan Tseng, Rosenstiel Post-Doctoral Fellow, Division of Applied Marine Physics.
- Chen Peng, Graduate Assistant, Division of Applied Marine Physics (MS obtained December 1992).