Experimental Support for Analyses of Coalescence

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The rate of coalescence of bubbles is important to the preparation and stability of foams, to the separation of minerals by froth flotation, and to the displacement of an unstable foam used for mobility control in the tertiary oil recovery processes.

When two bubbles are forced to approach one another in a liquid phase or when a bubble is driven through a liquid phase to a liquid-gas interface, a thin liquid film forms and begins to drain. As the thickness of the draining film becomes sufficiently small (about 1,000 Å), the effects of the disjoining pressure attributable to London-van der Waals forces and to any electrostatic double layer become significant.

Hahn et al. (1985) develop a hydrodynamic theory for the thinning of a liquid film between a small drop or bubble and a fluid-fluid interface. The analysis leads to the prediction of the coalescence time (rest time or time that the bubble appears to rest at the interface before coalescence occurs) under the influence of London-van der Waals forces, given only the appropriate physical properties and bubble radius. The predicted film profiles as functions of time are in reasonable agreement with those observed by Woods and Burrill (1972), Burrill and Woods (1973), and Liem and Woods (1974). However, Hahn et al. (1985) are relatively unsuccessful in using their theory to describe the coalescence times for nitrogen bubbles rising in various liquids observed both by Allan et al. (1961) and by MacKay and Mason (1963). Their assumption of immobile interfaces may be the cause of the overestimated coalescence times.

In considering the coalescence of a small bubble at a liquid-gas interface, Hahn and Slattery (1985) analyze a liquid film bounded by partially mobile parallel planes, recognizing the effects of the surface viscosities and of the London-van der Waals forces but ignoring the effects of interfacial tension gradients. They are able to predict the coalescence time for the bubble as a function of the system properties. This analysis is approximate, since it ignores the dimpling of the liquid film.

Hahn and Slattery (1986) take into account the dimpling of a liquid film formed as a small bubble approaches a liquid-gas interface, as well as the effects of the surface viscosities and the effects of the retarded London-van der Waals forces. Qualitatively, the results are consistent with those of Hahn and Slattery (1985) for a plane-parallel film. Quantitatively, there is a considerable difference. The plane-parallel film model is too superficial to give an accurate prediction for the coalescence time. Both analyses (Hahn and Slattery, 1985, 1986) conclude that if surface viscosities are sufficiently large, the interfaces bounding the film act as though they are immobile. For a large intermediate range of surface viscosities, the coalescence time is a strong function of surface viscosities.

In these analyses (Hahn et al., 1985; Hahn and Slattery, 1985, 1986), the effects of any electrostatic double layer were neglected. At sufficiently high concentrations of electrolyte, the double-layer repulsive forces are weak and they can be neglected (Osipow, 1962; Davies and Rideal, 1963; Scheludko, 1967).

Our objective is to test these results experimentally for a nitrogen bubble approaching a liquid-gas interface in solutions of dodecyl sodium sulfate having different concentrations of NaCl.

Experimental Method

Aqueous solutions of 3.47×10^{-4} M dodecyl sodium sulfate (99%, Fisher Scientific Co.) were employed. Sodium chloride (analytical reagent grade) was added to suppress the electrostatic forces in the film.

The coalescence time (rest time) and the diameter of each bubble were measured employing techniques and equipment similar to those used by Allan et al. (1961). A wild M7S zoom stereo microscope was focused on the liquid surface and the diameter of the bubble was measured using a calibrated scale in the eyepiece. All measurements were conducted at room temperature, about 26°C. In Table 1, we report the average coalescence times and standard deviations for 20 bubbles.

Discussion

In Figure 1 we show the average coalescence time for bubbles with radius 0.0625 cm as a function of C_{NaCl}, the molar concen-

Table 1. Experimental Measurements of Coalescence Time

		R_b, cm					
		0.0625		0.065		0.060	
C_{NaCl} M	γ mN/m	t_c s	σ s	t_c s	σ s	t_c s	σ s
0.0	70.27	>300	—	—	—	—	—
0.025	55.23	207.86	98.00	—	—	—	—
0.05	51.21	38.10	4.51	—	—	—	—
0.05	51.21	37.16	2.20	—	—	—	—
0.075	47.50	34.86	2.11	—	—	27.48	2.28
0.10	45.00	36.51	1.96	43.21	2.07	—	—
0.20	39.17	39.95	1.52	46.61	2.24	33.24	1.44
0.30	35.02	45.33	0.99	—	—	39.13	2.40
0.40	32.88	50.35	2.55	—	—	42.65	2.64
0.50	31.26	52.5	4.40	—	—	—	—

R_b, bubble radius
t_c, coalescence (rest) time
c_{NaCl}, molar concentration of NaCl
γ, surface tension
σ, standard deviation

tration of NaCl. These data are compared with the predictions of Hahn et al. (1985) for a dimpled film with immobile interfaces, of Hahn and Slattery (1985) for a plane-parallel film with partially mobile interfaces, and of Hahn and Slattery (1986) for a dimpled film with partially mobile interfaces. It is clear from this comparison that it is important to recognize both the mobility of the interfaces and the dimpling of the film.

In these analyses, London-van der Waals forces have been assumed to be retarded. Several authors (Kitchener and Prosser, 1957; Black et al., 1960; Sheludko et al., 1965; Churaev, 1974; Derjaguin et al., 1977) reported the approximate values of the

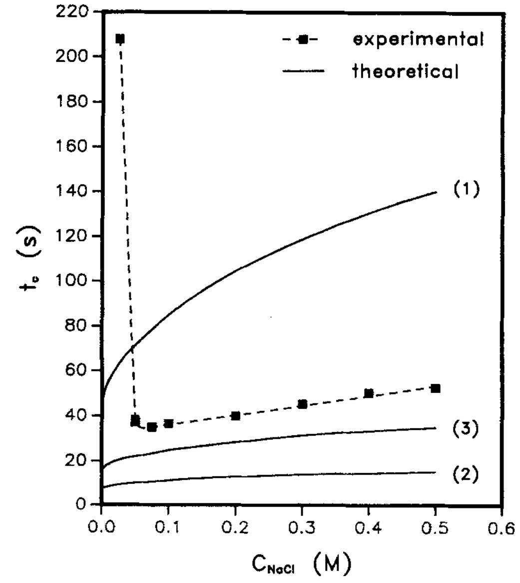

Figure 1. Coalescence time (rest time) t_c as a function of C_{NaCl} for bubble radius R_b = 0.0625 cm.
Comparison with predictions of:
(1) Hahn et al. (1985), $B = 10^{-19}$ erg · cm
(2) Hahn and Slattery (1985), $B = 10^{-19}$ erg · cm; $\kappa + \epsilon = 0.02$ mN · s/m
(3) Hahn and Slattery (1986), $B = 10^{-19}$ erg · cm; $\kappa + \epsilon = 0.02$ mN · s/m

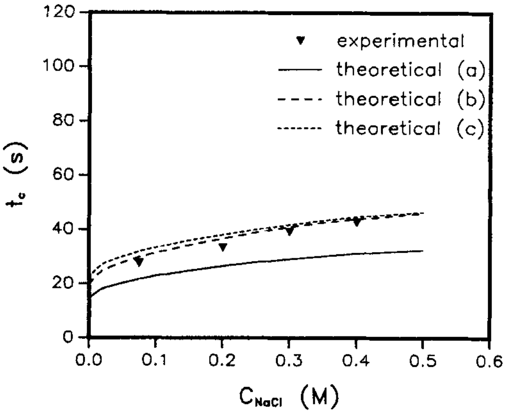

Figure 2. Coalescence time (rest time) t_c as a function of C_{NaCl} for bubble radius R_b = 0.60 cm.
Comparison with predictions of Hahn and Slattery (1986)
(a) $B = 10^{-19}$ erg · cm; $\kappa + \epsilon = 0.02$ mN · s/m
(b) $B = 10^{-19}$ erg · cm; $\kappa + \epsilon = 0.05$ mN · s/m
(c) $B = 2.0 \times 10^{-20}$ erg · cm; $\kappa + \epsilon = 0.02$ mN · s/m

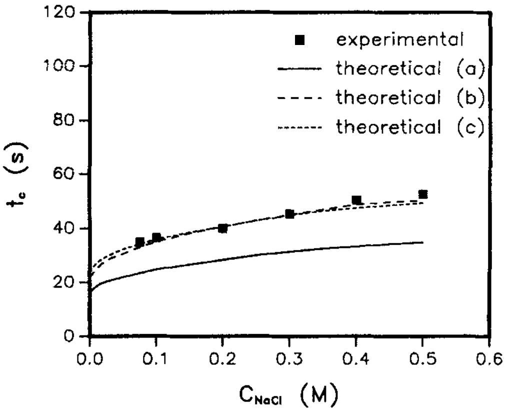

Figure 3. Coalescence time (rest time) t_c as a function of C_{NaCl} for bubble radius R_b = 0.0625 cm.
Comparison with predictions of Hahn and Slattery (1986)
(a) (b) (c) Data as in Figure 2

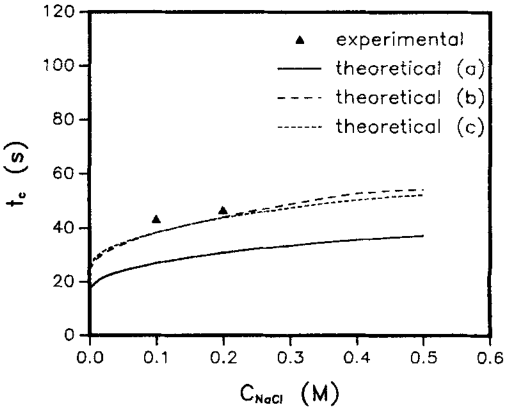

Figure 4. Coalescence time (rest time) t_c as a function of C_{NaCl} for bubble radius R_b = 0.065 cm.
Comparison with predictions of Hahn and Slattery (1986)
(a) (b) (c) Data as in Figure 2

London-van der Waals constant between two flat surfaces (Hahn et al., 1985, Eq. 13; Hahn and Slattery, 1985, Eq. 7; Hahn and Slattery, 1986, Eq. 12) as $|B| \sim 10^{-19}$ erg · cm. Note that B is always positive when two homophases approach each other, as in the case being considered here.

These analyses (Hahn et al., 1985; Hahn and Slattery, 1985, 1986) also assume that both interfaces have the same surfactant concentrations, surface tension, and surface viscosities. In general, we could expect that the freshly formed interface of the bubble would have a rapidly changing surfactant concentration as the result of diffusion and adsorption of surfactant from the adjacent continuous phase; the older interface that the bubble approaches could be expected to be nearly in chemical equilibrium with the continuous phase. For aqueous solutions of dodecyl sodium sulfate solution with sodium chloride added (Burcik, 1953; Owens, 1969; Caskey and Barlage, 1971), approximately 60% of the surface tension lowering (a convenient figure) occurs within 0.1 s. This suggests that for the system considered here, the characteristic time for diffusion and adsorption of surfactant into the interface (~0.1 s) is two orders of magnitude smaller than the coalescence time (~20 s) for the bubbles studied here, indicating that chemical equilibrium is attained rapidly.

The surface shear viscosity ϵ for this system is estimated to be less than 10^{-5} mN · s/m, since it could not be detected in our deep-channel surface viscometer (Wei and Slattery, 1976; Jiang et al., 1985). If κ denotes the surface dilatational viscosity, $\kappa + \epsilon = 0.02$ mN · s/m (Djabbarah and Wasan, 1982) in the absence of electrolyte. We did not confirm this, since this value of $\kappa + \epsilon$ would be outside the range of our capillary rise instrument (Stoodt and Slattery, 1984). Lacking further information, we accepted this value for $\kappa + \epsilon$ and we assumed it to be independent of C_{NaCl}.

The addition of NaCl in the solution causes both the electrostatic forces and the surface tension to be reduced. In the absence of NaCl, the bubble rested at the interface, sometimes as long as several hours without breaking. Figure 1 shows that the coalescence time first decreases dramatically as the concentration of NaCl increases, which is attributable to diminished electrostatic repulsive forces. With increasing concentration of NaCl, these experimental measurements almost parallel the theoretical predictions, suggesting that the effects of the electrostatic forces were indeed becoming negligible as more NaCl was added to the system. The increase of coalescence time with the concentration of NaCl is due to the decrease of surface tension, Table 1.

Figures 2–4 show better comparisons between our data and the theory of Hahn and Slattery (1986); these data can be obtained with minor adjustments to B or to $\kappa + \epsilon$.

Acknowledgment

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