

## Reply to “Comment on ‘Deformation of fluid interfaces under double-layer forces stabilizes bubble dispersions’ ”

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This paper is in reply to a criticism of a recently proposed explanation for bubble coalescence inhibition by electrolytes. We argue that the proposed deformation mechanism, demonstrably represented using classical Derjaguin-Landau-Verwey-Overbeek interaction potential (DLVO) theory [Phys. Rev. E **54**, 6551 (1996)] is more generally valid than suggested by the mean-field DLVO approximation. We argue that repulsive steric (hard-core) and polarization (image charge) effects are significant at high concentrations and will lead to bubble interfacial deformation. This, in turn, will influence bubble-bubble interactions giving rise to bubble dispersion behavior consistent with observations. [S1063-651X(98)05106-X]

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Craig, Ninham, and Pashley [1] have criticized a recently proposed explanation [2] for why bubbles cease to coalesce or are inhibited from coalescing in concentrated salt solutions. Underlying the proposal is the fact that the gas-water interface of bubbles is capable of severe deformation under repulsive surface forces; this deformation is a function of a bubble's Laplace pressure. The continuum Derjaguin-Landau-Verwey-Overbeek interaction potential (DLVO) model of the electrical double-layer force that was employed in Ref. [2] predicted behavior that is qualitatively consistent with observed coalescence phenomena in certain salt solutions. That is, coalescence inhibition—*when it is found to occur with certain electrolytes*—is well represented qualitatively by the deformation mechanism advanced by Miklavcic [2].

The deformation mechanism has now been misrepresented in the Comment by Craig *et al.*, who focus attention instead on the application of the DLVO theory. However, it was already admitted in Ref. [2] that this continuum model has limited applicability. Surface polarization effects are missing as are steric contributions due to the finite size of ions and even ion hydration effects. These contributions lead to more repulsive double-layer forces than predicted by DLVO theory [3,4], while the ion correlation contribution is attractive [5].

Recently published electrophoretic data indicate that the  $\zeta$  potential of bubbles is “of the order of only 1 mV” [6]. This is even lower than the estimate I suggested would give quantitative agreement with experiment [2]. The critical salt concentration at which the onset of coalescence inhibition occurs is experimentally found to be about 0.1M, at which concentration the continuum model of the electrical double layer has ceased to be valid. The ion correlation contribution is not expected to be significant for this surface potential, with monovalent electrolytes. The repulsive steric and image charge contributions, which become quite significant at small separations and which increase with increasing salt concentrations, are therefore dominant. It is quite likely that the resulting electrical double-layer force will dominate the van der Waals force, again giving rise to surface deformation, and to coalescence inhibition in the manner proposed in Ref. [2]. These contributions to the electrical double-layer force have not been considered by Craig *et al.* [1], and should most certainly be made the subject of future investigation.

Finally, I reiterate what has already been stated in Ref. [2], that specific ion effects *are* indeed important but were intentionally not entertained in that physical model. These must also be considered in any future undertaking if the puzzle, as to why some salts inhibit coalescence and others not, is to be solved.

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