

## COMMENTS

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

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In a recent publication it was suggested that a simple double-layer force could be used to explain the unexpected effect of electrolytes on reducing air bubble coalescence in aqueous solutions. We suggest here that this force cannot explain the observed behavior or the ion-pair specificity of the phenomenon, and that an adequate explanation has yet to be found. [S1063-651X(98)05306-9]

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A constant potential double-layer repulsion that increases with electrolyte concentration is utilized by Miklavcic [1] to induce bubble surface deformations and thereby explain the phenomenon of bubble coalescence inhibition that occurs upon addition of some electrolytes to water. This mechanism has previously been dismissed by one of us [2]. Acceptance of such an interpretation requires that a number of experimental facts be overlooked:

(i) Coalescence inhibition for 1:1 electrolytes only begins to occur at concentrations above about 0.1 M [3–5]. This concentration is two to four orders of magnitude higher than those considered by Miklavcic. Bubble coalescence inhibition is not observed at the lower concentrations considered by Miklavcic. The calculated data presented are therefore irrelevant to coalescence inhibition. The inference that this difficulty can be overcome by assuming that a low potential on the bubble surface is incorrect. At such low potentials, according to present theories, the interaction would then be dominated by attractive van der Waals forces and the net force between two bubbles would be attractive.

(ii) Coalescence inhibition is undiminished at electrolyte concentrations of several molar [3–7] where double-layer electrostatic forces are negligible relative to van der Waals attractive forces in the air-water-air system. The Miklavcic mechanism predicts that coalescence should occur readily at these high concentrations as electrostatic forces are highly screened and van der Waals forces dominate. This is contrary to observation.

(iii) A large number of electrolytes have little or no effect at all on bubble coalescence [1,3,4]. A Derjaguin-Landau-

Verwey-Overbeek interaction potential (DLVO) treatment cannot distinguish electrolytes that have an effect from those that do not. Indeed, electrolytes that are unable to inhibit bubble coalescence such as NaClO<sub>4</sub>, Na acetate, and HCl would behave in the same manner as electrolytes that are able, such as NaCl and HClO<sub>4</sub>. The specific ion effects observed in bubble coalescence are dramatic and are not encompassed by DLVO theory [8]. Indeed, the DLVO theory has been shown to be quite invalid theoretically around and above concentrations of 0.1M.

(iv) At the electrolyte concentrations required to inhibit coalescence, film breakup occurs at separations orders of magnitude larger than the range of electrostatic double-layer forces. Indeed, in pure water, films formed between a bubble and a hydrophobic flat surface are unstable and rupture at separations of 1000 Å and greater [9–14]. At such separations, in concentrated electrolyte solutions, any conventional DLVO electrostatic force is irrelevant. It is for this reason that such a mechanism was dismissed [1,3,4]. No considerations that postulate theoretical boundary conditions can overcome this difficulty.

Electrostatic double-layer forces cannot describe the phenomenon either qualitatively or quantitatively. The theory is also deficient in the postulate that the air-water interface behaves as an ideal constant potential surface. More importantly specific ion-pair-combining rules [3,4] that systematize the bubble coalescence behavior of electrolytes are not addressed. The problem is difficult and unresolved. New insights into other areas of importance in colloid science can be expected if and when an adequate explanation emerges.

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