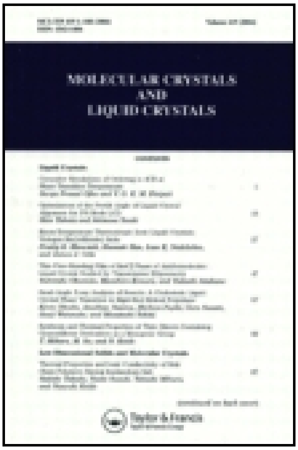

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Van Der Waals Potential In Coalescing Emulsion Drops With Liquid Crystals

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VAN DER WAALS POTENTIAL IN COALESCING EMULSION DROPS WITH LIQUID CRYSTALS

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Abstract The influence of a liquid crystal on the Van der Waals potential for the coalescence of emulsion droplets was calculated.

INTRODUCTION

Although the existence of liquid crystals in emulsions had earlier been suggested (1, 2) and their importance for the rheological properties had been pointed out, the direct influence of their presence on emulsion stability was first demonstrated in 1969 (3). This contribution was followed by confirmatory investigations on different model systems (4) and by application of the mechanism in different areas (5). The present report is concerned with the influence of an adsorbed lamellar liquid crystal on the Van der Waals distance dependence between two coalescing emulsion droplets in order to clarify the main reason for the pronounced increase of emulsion stability (4) arising from the presence of a liquid crystal.

RESULTS AND DISCUSSION

The coalescence is postulated to take place by successive removal of bi-layers leading to a stepwise approach of the two droplets and ending in a final thin layer and coalescence (Fig. 1). The potential of the removed layers is assumed not to change during the process in accordance with the planar case (6).

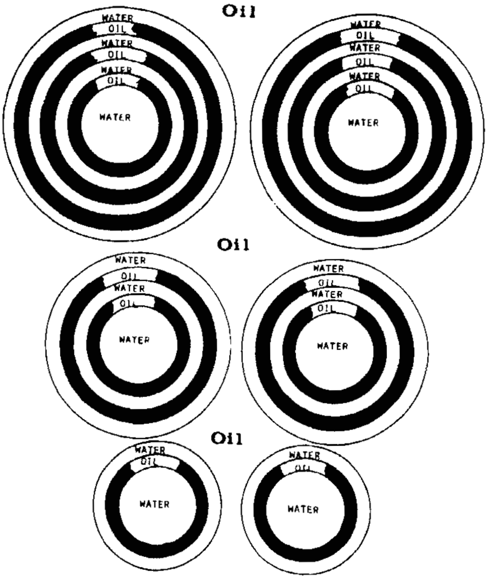

FIGURE 1 The change of Van der Waals potential during the coalescence process for emulsion droplets covered with a lamellar liquid crystal was calculated using a model system with consecutive removal of 2 layers.

The calculations used a generalization of Vold's formula (7) with the Hamaker approach; a more detailed study using the Parsegian approach (8) will be published. The Vold formula in many-layered form reads

$$
\begin{aligned}
V= & -\frac{1}{12}\sum_{i=1}^{2n+1}\sum_{j=1}^{2n+1} a_i a_j H_{ij} = \\
& -\frac{1}{12}\left(A_w^{1/2}-A_o^{1/2}\right)^2 \left\{ \sum_{i=o}^{n-1} \left[H\left(\frac{d+2i(p+q)}{2[R+(n-i)(p+q)]},1\right) + \right.\right. \\
& \left. H\left(\frac{d+2i(p+q)+2p}{2[R+(n-i)(p+q)-p]},1\right)\right] + H\left(\frac{d+2n(p+q)}{2R},1\right) \\
& + 2\left[\sum_{i=1}^{n-1}\sum_{j=i+1}^{n} H\left(\frac{d+(i+j)(p+q)-2q}{2[R+(n-j)(p+q)+q]},\right.\right. \\
& \left.\frac{R+(n-i)(p+q)+q}{R+(n-j)(p+q)+q}\right) + \sum_{i=1}^{n}\sum_{j=i+1}^{n+1} \left[H\left(\frac{d+(i+j-2)(p+q)}{2[R+(n-j+1)(p+q)]},\right.\right. \\
& \left.\frac{R+(n-i+1)(p+q)}{R+(n-j+1)(p+q)}\right) - H\left(\frac{d+(i+j-1)(p+q)-q}{2[R+(n-j+1)(p+q)]},\right. \\
& \left.\frac{R+(n-i)(p+q)+q}{R+(n-j+1)(p+q)}\right) - H\left(\frac{d+(i+j-2)(p+q)-q}{2[R+(n-j+1)(p+q)+q]},\right. \\
& \left.\left.\left.\left.\frac{R+(n-i+1)(p+q)}{R+(n-j+1)(p+q)+q}\right)\right]\right]\right\}
\end{aligned}
$$

The result showed a drastic reduction of the potential decrease in the initial states of the coalescence process after the flocculation step (Fig. 2).

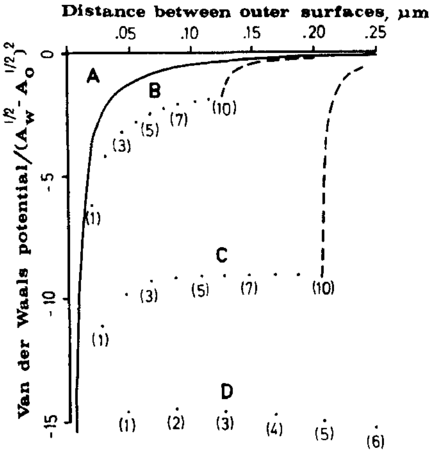

FIGURE 2 The Van der Waals potential reduction was extremely small during the coalescence process for droplets covered with a liquid crystal (B-D). Drop radius = 1 µm. Hydrocarbon layer thickness 50Å (B-D). Water layer thickness 10Å (B), 50Å (C) and 150Å (D).

For the case of water layers of 10Å (Fig. 2B) the removal of the first layer gave rise to a potential drop of only 0.5% of the total VdW potential for flocculation and coalescence.

Removal of the first three layers from droplets with a water layer thickness of 50Å ((10)-(7) Fig. 2C) actually caused an increase of the VdW potential by about 1%, an increase that is more pronounced in the case of aqueous layers of 150Å (Fig. 2D).

These results should not be interpreted as a proof of thermodynamical stability of the flocculated state of an emulsion, but rather serve further to emphasize the drastic modification of the Van der Waals potential by the presence of a layered structure between two emulsified droplets. The initial change of Van der Waals potential, when the outer layers are removed, is still found to be extremely small when a model is employed which is closer to reality than the present one.

The potential drop in the flocculation process is high for the droplets covered with a liquid crystal; in Fig. 2D the flocculation potential drop is equal to the total VdW potential loss during destabilization. However, this increased flocculation potential will not serve to destabilize the emulsion to a measurable degree; recent results (6) show that the kinetic energy of the two approaching drops is of minor influence for the stability. The viscous resistance becomes extremely high at short distances and the kinetic energy is absorbed in the high shear field localized mainly in the perpendicular central plane between the droplets.

Combining the results on the viscous resistance at close distance between two approaching droplets (6) with the present results emphasizing the pronounced modification of the Van der Waals potential during the coalescence, it appears reasonable to conclude the latter effect to be mainly responsible for the pronounced stability of emulsions containing liquid crystals.

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