The Effect of Nanoparticle Hydrophobicity on the Rheology of Highly Concentrated Emulsions

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Abstract:
A series of fumed silica nanoparticles were used as an additional emulsifier for highly concentrated (HC) water-in-oil (W/O) emulsions. These nanoparticles, with different hydrophobicity index (HI) in the 0.60 – 1.34 and HI > 3 range, were mixed with the conventional low molecular weight surfactant, sorbitan monooleate (SMO), in the oil phase prior to the emulsification process. The rheological properties of these emulsions were measured and compared with the properties of emulsions stabilized with SMO alone. In the mixed emulsifier system, the changes in rheological parameters were clearly expressed as a function of HI. The mixture of silica nanoparticles and SMO significantly increases the yield stress and plateau modulus of fresh emulsion, compared to the SMO only system. The effect was found to be more pronounced with a decrease in the HI. This is probably related to the reduction in micelle content with the decrease in HI, owing to a concomitant increase in the amount of SMO adsorbed onto the particle surface. Then, interestingly, the Foudazi-Masalova model recently developed for surfactant-stabilized highly concentrated emulsions (HCE) was found to describe successfully the rheological behavior of emulsions in the presence of a mixture of surfactant and fumed nanosilica.

Zusammenfassung:
Mehrere pyrogene Silika-Nanopartikel wurden als zusätzliche Emulgierungsmittel für hochkonzentrierte (HC) Wasser-in-Öl (W/O)-Emulsionen verwendet. Diese Nanopartikel, die unterschiedliche Hydrophobizitätsindizes (HI) im Bereich von 0.60 bis 1.34 und HI > 3 besitzen, wurden mit einem konventionellen, niedermolekularen Surfaktanten (Sorbitanmonooleat, SMO) in die Ölphase vor dem Emulsifikationsprozess gemischt. Die rheologischen Eigenschaften dieser Emulsionen wurden gemessen und mit den Eigenschaften der mit dem SMO alleine stabilisierten Emulsionen verglichen. Bei den gemischten Emulgierungsmitteln waren die rheologischen Eigenschaften eindeutig vom HI-Wert abhängig. Die Mischungen der Silika-Nanopartikel und dem SMO erhöhten in signifikanter Weise die Fließspannung und den Plateau-Modul der frischen Emulsion im Vergleich zu dem System, das mit SMO alleine stabilisiert wurde. Der Effekt trat deutlicher bei einem geringeren HI-Wert auf. Dies steht wahrscheinlich mit der Abnahme des Mizellengehaltes aufgrund der als Begleiterscheinung auftretenden Zunahme des SMO-Gehalts in Zusammenhang, das auf der Partikeloberfläche adsorbiert ist. Weiterhin beschreibt interessanterweise das Foudazi-Masalova-Modell, das kürzlich für mit durch Surfaktanten-stabilisierte hochkonzentrierte Emulsionen (HCE) entwickelt wurde, das rheologische Verhalten der Emulsionen mit Surfaktanten und pyrogenen Nanosilikapartikeln.

Résumé:
Une série de nanoparticules de fumée de silice a été utilisée comme émulsifiant additionnel d'émulsions eau-dans-huile (W/O) concentrées. Ces nanoparticules, possédant différents index d'hydrophobicité (HI) dans la gamme 0.6 – 1.34 et HI > 3, ont été mélangées avec du surfactant conventionnel de bas poids moléculaire, du mono oléate de sorbitane (SMO), dans une phase d'huile, avant le procédé émulsifiant. Les propriétés rhéologiques de ces émulsions ont été mesurées et comparées avec celles des émulsions stabilisées seulement par le SMO. Dans le système d'émulsifiant mixte, les changements des paramètres rhéologiques avec le HI sont clairement révélés. La mixture de nanoparticules et de SMO augmente significativement la contrainte seuil et le module plateau de l'émulsion fraîche, comparé au système avec le SMO seul. L'effet s'est avéré plus prononcé lorsque le HI décroît. Ceci est probablement lié à la réduction du nombre de micelles avec la baisse du HI, du à l'augmentation correspondante de la quantité de SMO adsorbé sur la surface de la particule. Ensuite, de manière intéressante, le modèle Foudazi-Masalova récemment développé pour les émulsions concentrées stabilisées par du surfactant (HCE), décrit avec succès le comportement rhéologique en présence du mélange de surfactant et de fumée de silice.

Key words: emulsions, rheology, fumed nano-silica, surfactant

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