

Wettability of Complex Fluids and Surfactant Capped Nanoparticle-Induced Quasi-Universal Wetting Behaviour

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Supplementary Information

Scheme S1. Determination of polar and dispersive components of surface energy for substrates considered in the present study.

The degree of wettability, usually characterised by equilibrium contact angle, depends on the interfacial interactions at the molecular scale^{1, 2}. These interfacial interactions are governed by the gross interfacial energies of all the interfaces often denoted as the surface energy³. Owens Wendt method, one of the most widely used and recognised method; uses contact angle data in order to measure the interfacial energy (surface free energy) in terms of polar and dispersive interactions with test fluids having known polar and dispersive components of surface tension^{2, 4}. The polar and dispersive components of surface tension of common test fluids are well characterised and reported. DI water (in situ purified) and dimethyl sulphoxide

(DMSO) (99% pure, Avra synthesis, India) have been considered as the test fluids and their properties have shown in table S1. A detailed description of substrate preparation and method of measurement is provided in the main article.

Table S1: Polar and disperse components of test fluids

Sl. No	Test fluid	Total surface tension (mN/m)	Dispersive component (mN/m)	Polar component (mN/m)	Reference
1.	Water	72.8	22.6	50.2	1, 3, 6
2.	DMSO	44	36	8	1

Owens Wendt proposed the below relation based on Fowkes proposal of partitioning the surface energy into components. They proposed the following relation ^{1, 5}

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s^d \gamma_l^d)^{0.5} - 2(\gamma_s^p \gamma_l^p)^{0.5} \quad (1)$$

Where γ_{sl} is solid liquid interfacial tension, γ_s is the solid surface energy and γ_l is the liquid surface tension, γ_s^d and γ_s^p represents the dispersive and polar components of the solid surface energy and similarly the γ_l^d and γ_l^p represents the dispersive and polar components of the liquid counterpart. The approach by this method considered all the interactions except the dispersive interactions as polar.

$$\gamma_{sl} = \gamma_s - \gamma_l \cos \theta \quad (2)$$

Combining equation (1) and (2), we will get a linear equation of the form $y=mx + C$ can be arrived at as shown in equation below:

$$y = \frac{\gamma_l(1+\cos\theta)}{2\sqrt{\gamma_l^d}} = \underbrace{\sqrt{\frac{\gamma_s^p}{\gamma_l^d}}}_{B} * \underbrace{\sqrt{\gamma_s^p} + \sqrt{\gamma_s^d}}_{A} \quad (3)$$

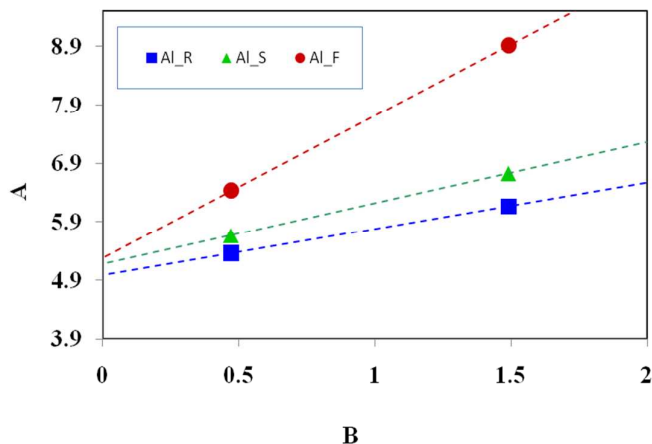


Figure S1. The evaluation of surface free energy for different aluminium substrates considered in the present study using equation (3).

So, the square of the slope will give the polar component of surface energy and the square of intercept of the linear equation will give the dispersive component of surface free energy of the substrate. Based on the equation (3) and making use of contact angle data and the dispersive and polar components of surface tension of test fluids from literature, the polar and dispersive components of the substrates are found out and are illustrated in figure S1 and figure S2.

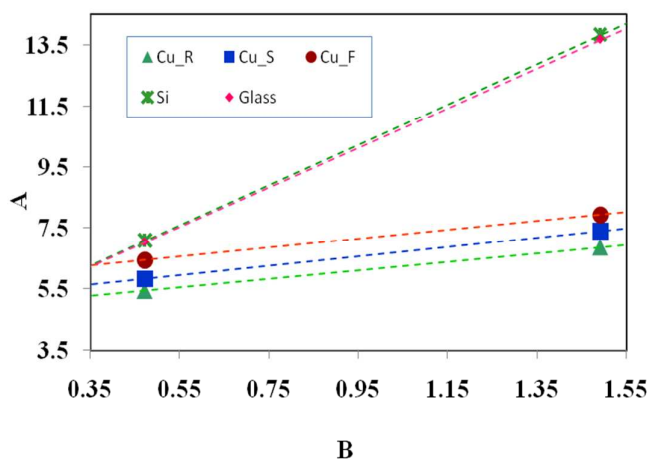


Figure S2. Calculation of surface free energy for different copper substrates, Silicon wafer and glass substrates.

The polar and dispersive components of different substrates obtained are represented in figure S3 and S4.

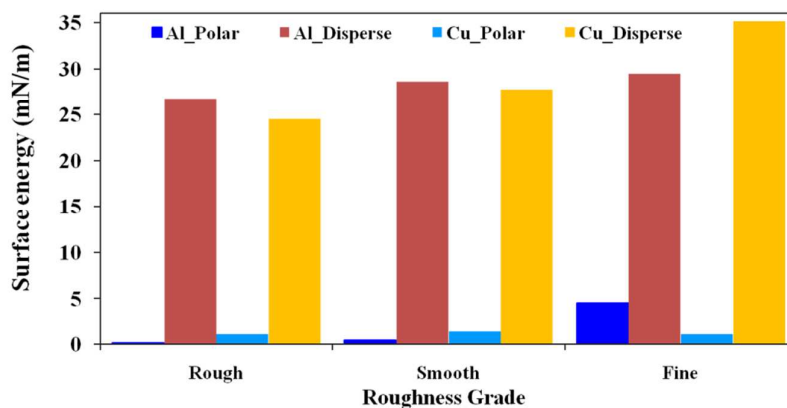


Figure S3. Polar and dispersive components in copper and aluminium substrates considered in the present study.

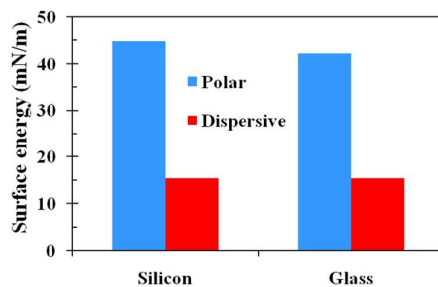


Figure S4. Polar and dispersive components in case of silicon and glass substrate.

Scheme S2. Wetting characteristics of aqueous surfactants (SDS, CTAB and DTAB)

The wetting characteristics of surfactants has been a topic of interest to research community for the past few decades and there are numerous studies on the dynamics of wetting, dewetting etc. The present study focuses on the above mentioned surfactants only in order to understand the effect of surfactants in a combined colloidal system. Figure S5 (a) shows the equilibrium static apparent contact angle of SDS on different grades of aluminium substrates. The droplet volume has been calculated in the initial transient phase of droplet spreading before reaching the equilibrium contact angle in order to ensure that the effect of droplet evaporation is negligible during the transient spreading stage (the maximum volume change observed being 7.9% during the droplet spreading span, not shown in the results). With the

increase in surfactant concentration, the contact angle decreases and this is the general trend reported in literature as well.

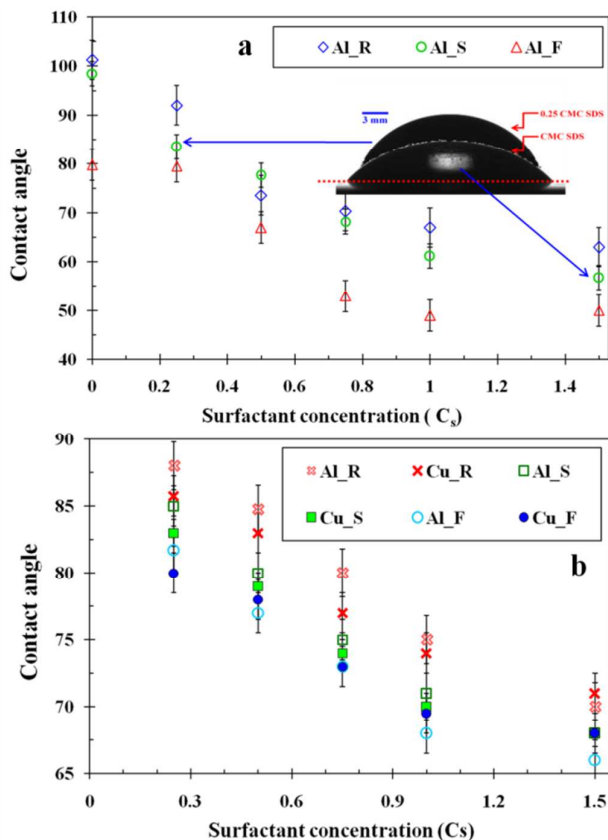


Figure S5 (a) Effect of SDS concentration on different surface grades of aluminium and (b) Effect of CTAB concentration on aluminium and copper surfaces for different grades of surface roughness.

Figure S5 (b) illustrates the variation in contact angle for cationic surfactant CTAB on aluminium as well as on copper substrates. The effect of unstructured roughness is clearly evident as it can be observed that on comparatively uniform smooth surface the spreading is more and the droplet attains a lower equilibrium contact angle. The uniform surface texture with enhanced surface energy results in better adhesion and attains a lower contact angle. The nature of variation of contact angle is observed to be similar as that of SDS both in the pre and post micellar regions. Similarly, Fig. S6 (a) illustrates the effect of surface roughness grade on the apparent equilibrium contact angle at various concentration of SDS for copper substrate. The nature of variation is exactly similar to the aluminium substrate. A common characteristic feature evident in the behaviour on both aluminium and copper substrate is that

for the finer grade of surface roughness the change in contact angle with the increase in concentration is higher compared to the relatively course surface grades. The change is much steeper when marching towards the micellar concentration. The finer grades facilitate an easy propagative front of the three phase contact point because of enhanced chances of adsorption of surfactant molecules to the substrate.

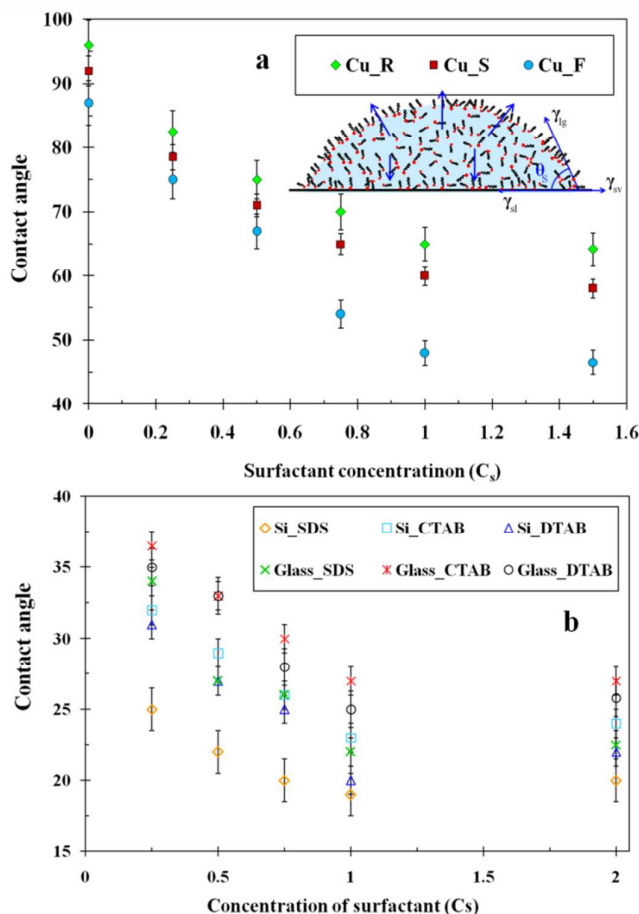


Figure S6 (a) Effect of surface grade of copper and surfactant concentration on equilibrium contact angle of aqueous SDS solution (b) Nature of variation of contact angle on Silicon (represented as Si) and Glass Substrate for SDS, CTAB and DTAB surfactants at various concentration levels.

A quantitative figure of nature of variation of contact angle of all the surfactants on silicon and glass, which are having a more uniform surface topography and hydrophilic in nature, is illustrated in Fig. S6 (b). The values reported are the equilibrium contact angle after the initial spreading stage. However, the surfactant molecules will exhibit preferential adsorption characteristics towards the gas-liquid and solid-liquid interface assuming that the

solid-gas interface remains unaffected by surfactant adsorption. The preferential adsorption characteristics depend on the nature of the surfactant and its affinity to the particular interface (as illustrated in Fig. S6 (a)). Moreover as the concentration increases, the steric hindrance modulates the adsorption characteristics⁷. As the concentration of the surfactant grows more than the CMC ($C_s > 1$), micelle starts to form in the solutions. Though the post micellar aqueous solutions can be considered as nanosuspension system, the present study is not focusing on concentrations higher than the CMC as the present objective is to understand the effect of surfactant capped nanoparticle suspension on the wettability.

Scheme S3. Wetting characteristics of only colloidal suspensions of only nanopartilces (Al₂O₃ and ZnO nanoparticles)

Figure S7 (a) illustrates the response of the equilibrium contact angle with respect to the change in particle concentration for Al₂O₃ nanofluids and Fig. S7(b) is that of ZnO nanofluids on aluminium and copper substrates.

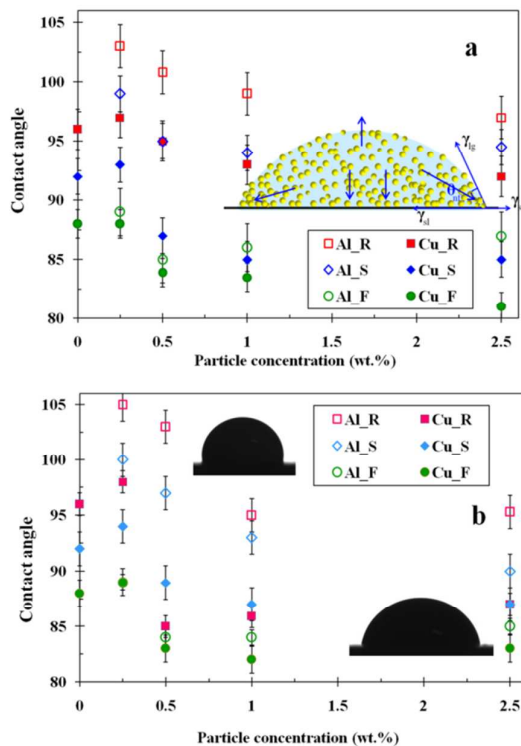


Figure S7 (a) Variation of equilibrium contact angle of Al₂O₃ nanofluid on different grades of aluminium and copper substrate (inset figure blue arrow indicates the particle migration and preferential adsorption to interface) (b) Variation in contact angle for ZnO nanofluid on aluminium and copper substrates.

Reference

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