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Conference Paper

Effect of Surfactant upon Capillary Adhesion in Four-phase Systems*

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Liquid bridges of aqueous sodium dodecyl sulphate solutions with different concentration between polytetrafluoro ethylene and pyrex glass surface have been experimentally investigated. The drop distribution isotherms are of the same type, their general shape being independent of the surfactant concentration but the characteristic points as the critical drop mass for total adherence and the constant drop mass corresponding to the steady state strongly depend on the surfactant concentration. The stability of the bridges as well as the formation of satellite droplets after breakdown of the bridge have been interpreted in terms of capillary waves. A simple energetic model consideration is proposed to explain effects caused by hysteresis.

INTRODUCTION

Capillary adhesion between two solids occurs if their surfaces are attracted by capillary forces due to the presence of a liquid bridge that fills the small gap between the surfaces. The bridge is surrounded by a second fluid phase (either the saturated vapour of the bridge liquid or a second liquid being immiscible with it) and the liquid/fluid interface meets both of the solid surfaces, exhibiting in the general case a finite contact angle on each of them. The solids can be of similar or dissimilar nature and both their position and geometry can arbitrarily be chosen. However, a mathematical analysis requires some restrictions with respect to the geometry as, e. g., two spheres¹, a sphere and plate², two parallel plates³, etc.

Apart from the obvious academic interest, liquid bridge type interfacial systems are of paramount importance for many practical fields like powder technology, printing processes, enhanced oil recover, capillary condensation in porous bodies and many more. That is why there has recently been a permanent interest in these systems opening a new field in the area of classical capillarity^{4,5}.

Of major importance of the properties of a liquid bridge is its mechanical (or Laplace) stability, i. e., its resistance against perturbances in the geometrical configuration due to mechanical influences, e. g., changing the volume

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of the liquid or varying the distance of separation or the location of the solid surfaces. A liquid bridge is mechanically stable if, upon changing the above parameters, the system is able to get into another geometrical configuration such that the Laplace equation for curved fluid interfaces is satisfied and the boundary conditions, as given by the contact angles at which the fluid interface meets the solid surfaces, are still met.

Closely connected with the mechanical stability is the distribution of the bridge-forming liquid among the two solid surfaces adjacent to it after breakdown of the bridge. Furthermore, valuable information can be obtained also by studying the mechanism and kinetics of both the formation and the breakdown, taking also non-equilibrium configurations into account.

From a theoretical point of view it is, of course, indifferent whether the fluid interface is a liquid/gas one (simple bridges) or a liquid/liquid one (double bridges). Nevertheless, if one is interested in studying experimentally the influence of gravity, double bridges are preferred, for, taking two (immiscible) liquids of equal density, the gravity free case can be realised which makes the theoretical evaluation of experimental data relatively simple. The other advantage of double bridges is that, due to the relatively lower mobility of the liquid/liquid interface comparing to that of the liquid/gas interface, the elementary processes during both formation and rupture of the bridge like adhering, spreading, displacement of the three-phase-line, thinning and neck-formation, formation of satellite droplets, etc. are much more slower than with single bridges. This is important from the experimental point of view because one can follow these processes by normal photographic procedure whereas for single bridges high frame-frequency cinematography (over 1000 frames per second) is needed.

In previous studies⁶⁻¹¹ we have reported a number of results concerning single bridges including also force measurements using the plate-plate geometry, and very recently we also investigated the mechanical stability of double bridges using the plate-plate geometry¹². In the present paper we are dealing with double bridges of the plate-sphere geometry with particular emphasis on the effect of a surfactant upon stability, distribution, hysteresis effects and mechanism of breakdown.

EXPERIMENTAL

Materials

Polytetrafluoro ethylene (PTFE, DuPont) was used as the substrate (bottom) surface and pyrex glass spheres (diameter 22 mm) as the adherent (top) surface. The polymer plate was rinsed in boiling acetone and washed in boiling distilled water, and the surface purity was checked by measuring the advancing contact angle of water ($114 \pm 2^\circ\text{C}$). A similar procedure was applied for the glass spheres.

The surfactant was sodium dodecyl sulphate (SDS, Merck). The commercial pure product was dissolved in and crystallized from ethanol-benzene mixtures and the purity was controlled by measuring the stability of thin films of the surfactant solutions according to our method as described earlier¹³. The c.m.c was determined from the concentration dependence of both the surface tension and the specific electric conductance of the solutions, and was found to be $8.1 \text{ mmol} \cdot \text{dm}^{-3}$. The organic liquid was *n*-octane, a Merck product which was used after distillation in vacuum and saturation with the aqueous phase. The aqueous surfactant solutions were also made from distilled water which was saturated with the organic liquid. The concentration was varied over a broad range, c/c_M being between 0.5 and 5.0, where c is the actual concentration, and c_M the c.m.c.

Measuring method

The bridge was formed of drops (volume 10 to 500 μm^3) of the surfactant solution between the horizontal PTFE plate and the glass sphere. The measuring cell was first filled up with the organic liquid and the drops were placed on to the polymer surface using a Hamilton microsyringe. After spreading equilibrium was reached, the holder with the plate was raised by a fine screw (Figure 1.) until contact of the drop with the sphere occurred. The shape of the capillary surface was photographed at each distance and the force was measured by a Beckman electronic microbalance. From the pictures the contact angle, the radius of the contact area and the co-ordinates of the meridian profile were determined. Each configuration belonging to a given separation was measured by both increasing and decreasing the bridge height, in order to get information about hysteresis effects. The separation was varied until breakdown of the bridge has taken place and the distribution of the bridge liquid after rupture was determined by the microbalance.

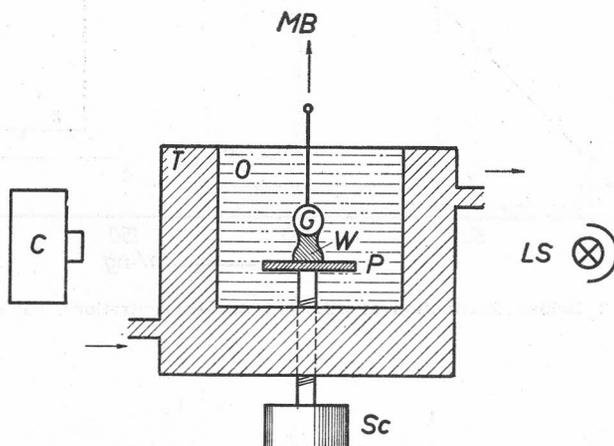


Figure 1. Measuring cell. W water bridge O octane, P Teflon plate, G glass sphere, MB microbalance, Sc fine screw, T thermostat, C camera, LS light source

RESULTS

The mechanical stability of the systems was characterized by the bridge distribution (BD) isotherms as described earlier. Figure 2. shows the BD curves obtained at different SDS concentrations. These curves are of the mass dependent type, i. e., up to a critical mass of the bridge liquid, m_{crit} , there is total transfer to, or complete displacement by, the adherent (top) surface whereas for $m > m_{\text{crit}}$ breakdown occurs. As it was so far found for all systems, in this region the distribution is such that the transferred mass (m_2) of the liquid becomes a constant ($m_{2, \text{st}}$ for $m > m_{\text{crit}}$) independently of the total bridge mass, i. e., a steady state is reached. Both m_{crit} and $m_{2, \text{st}}$ are strongly dependent on the surfactant concentration (Figures 3. and 4.). Also was measured the critical bridge height (d_{crit}) at which rupture of the bridge takes place. In Figure 5. the dimensionless quantity d_{crit}/h_0 (h_0 being the initial drop height prior to the formation of the bridge) is plotted against the relative concen-

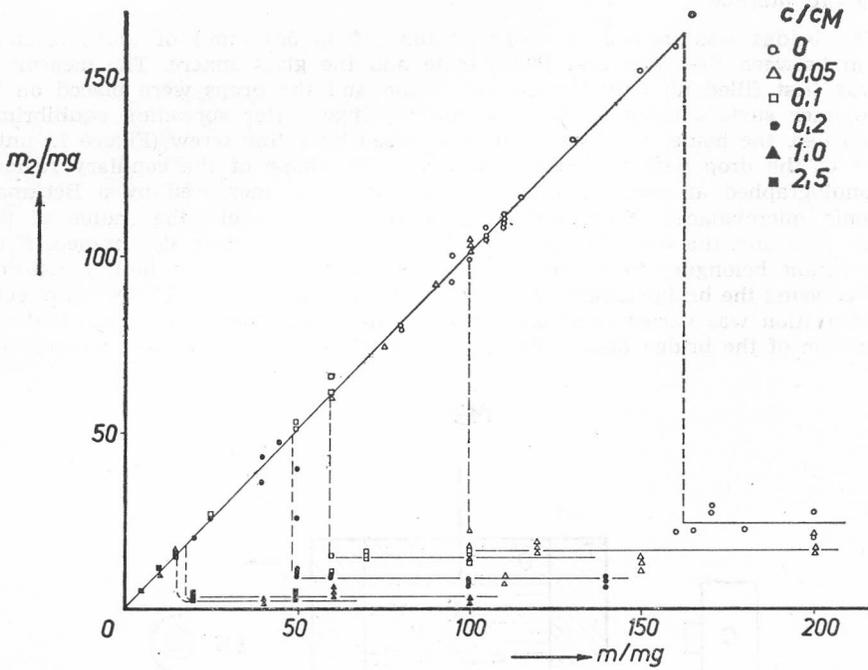


Figure 2. Bridge distribution at different SDS-concentrations, c_M : c. m. c.

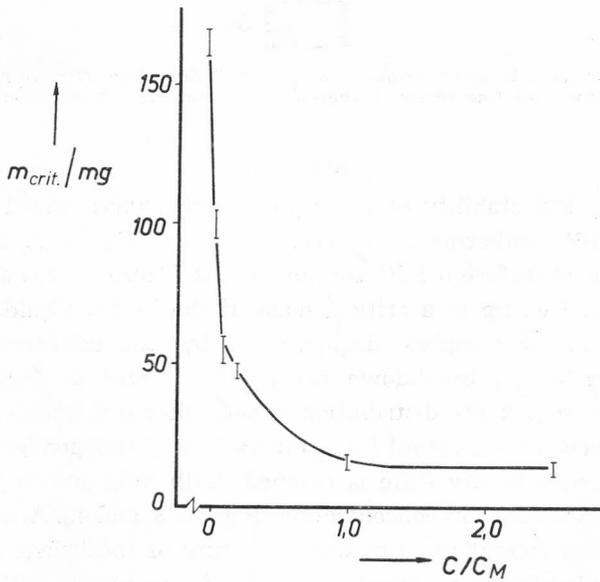


Figure 3. Dependence of m_{crit} on the relative SDS-concentration

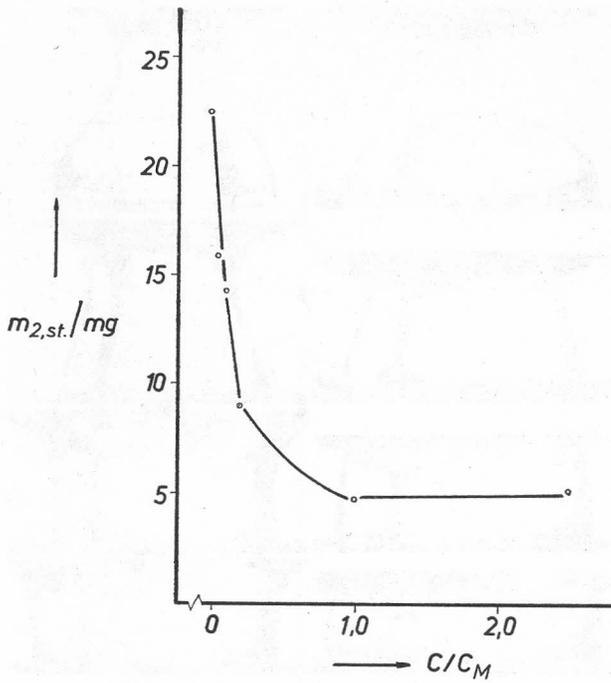


Figure 4. Dependence of $m_{2,st.}$ on the relative SDS-concentration.

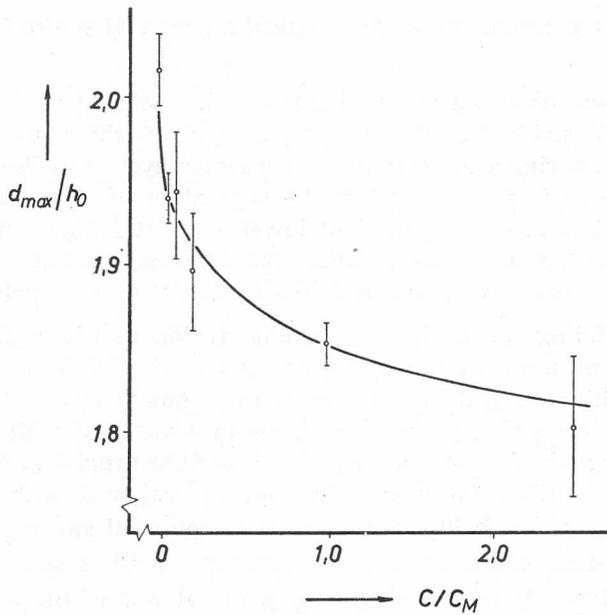


Figure 5. Dependence of the relative bridge height for breakdown on the relative SDS-concentration.

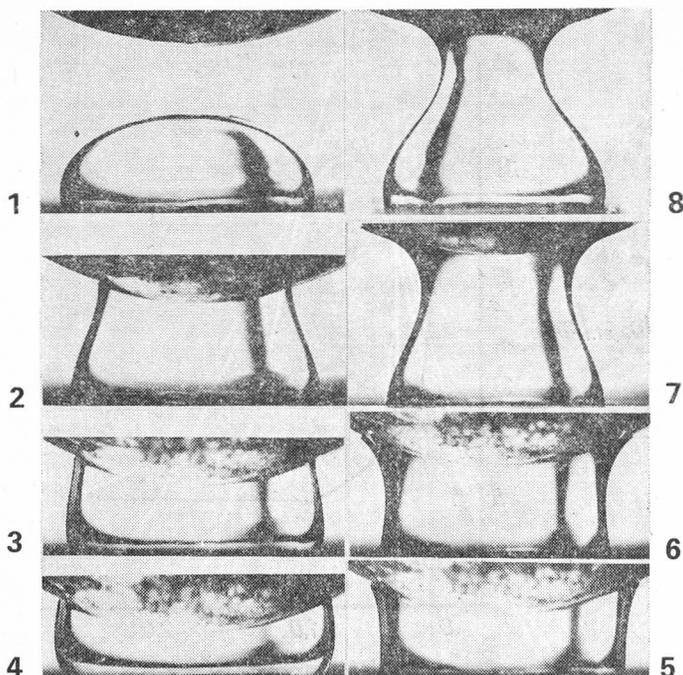


Figure 6. Hysteresis during a compression-expansion cycle. $V = 100 \text{ mm}^3$; $c = 0.2 c_M$.

tration c/c_M . It is apparent that c_M is a critical concentration also for the bridge stability.

Hysteresis was observed by varying the bridge height in the region where the bridge is still stable. The photo series in Figure 6. shows the shape of the capillary surface during a compression — expansion cycle, and Figures 7. and 8. the capillary force is plotted against the separation of the solids. One sees that hysteresis is more pronounced at lower than at higher surfactant concentration but, at the same concentration, the differences between compression and expansion forces become less and less by repeating the cycle.

While expanding the bridge, the middle region of the capillary surface becomes more and more negatively curved, giving rise to the neck-formation. At a certain critical height, the neck is thinning out to form a thin filament, and the mechanical stability suddenly drops to a value at which breakdown takes place. From the filament a very small satellite droplet is formed which moves in vertical direction until, after several contacts with each of the macroscopic rests of the bridge adhering on to the solid surfaces, coalescence occurs. The life-time of the satellite droplets was found to be of the order of seconds, in contrary to single bridges for which it was of the order of milliseconds. The diameter of the satellite droplets was found to be strongly dependent on the surfactant concentration.

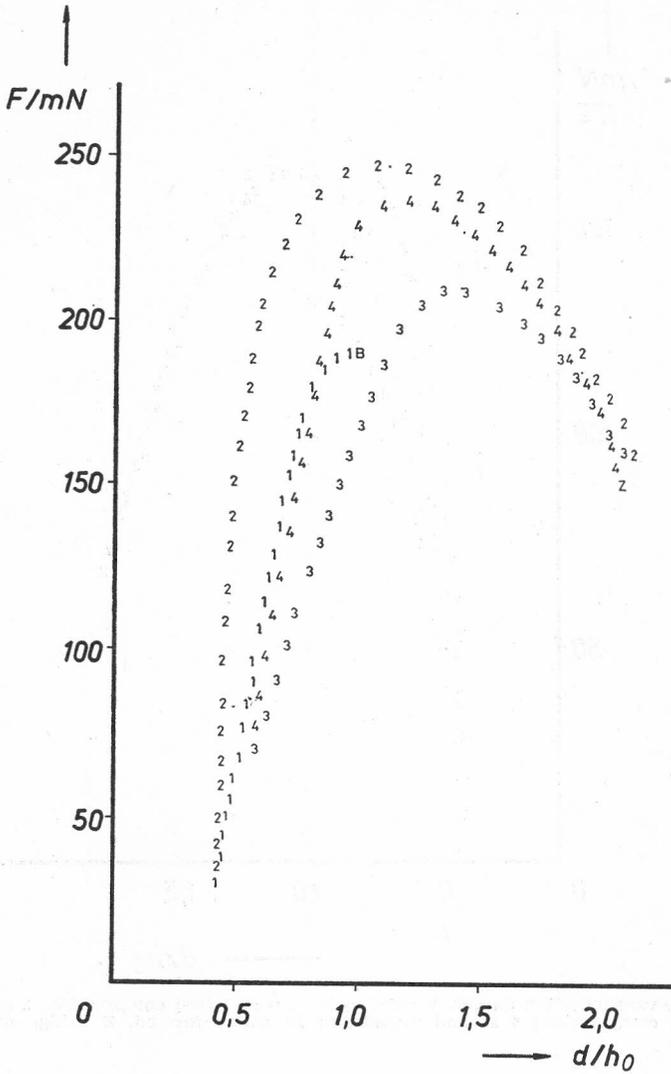


Figure 7. Force vs. separation curves. $V = 100 \text{ mm}^3$; $c = 0.1 C_M$ 1 first compression; 2 first expansion; 3 second compression; 4 second expansion; B bridge formed, Z bridge disrupted.

DISCUSSION

The general condition for the Laplace type stability of fluid interfaces is given, according to Everett and Haynes¹⁴ by

$$dA^{\text{eff}}/dV = \text{const.} \tag{1}$$

where V is the volume of the liquid, and the effective area, A^{eff} , is defined as

$$A^{\text{eff}} = A^{\text{LF}} - A^{\text{LS}} \cos \theta \tag{2}$$

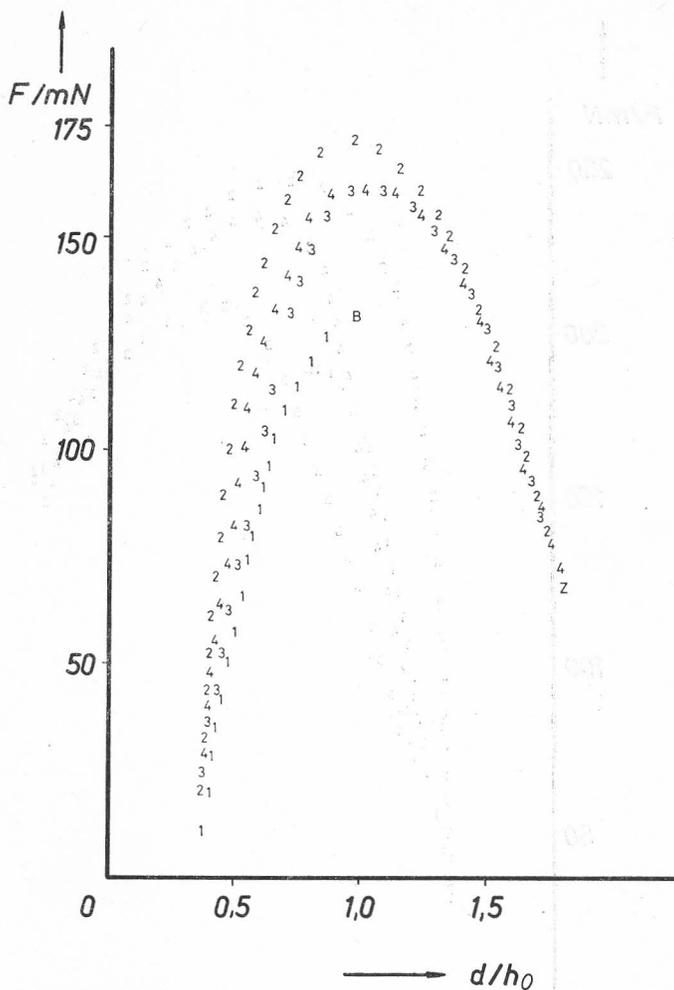


Figure 8. Force vs. separation curves. $V = 100 \text{ mm}^3$, $c = c_M$ 1 first compression; 2 first expansion; 3 second compression; 4 second expansion; B bridge formed, Z bridge disrupted.

here A^{LF} and A^{SL} , respectively, are the fluid and the solid/liquid interfacial areas, and θ is the equilibrium contact angle at the solid/liquid/fluid boundary line as given by the Young's equation.

For double bridges, Eq. (2) is to be written as

$$A^{\text{eff}} = A^{L_1 L_2} - (A^{S_1 L_1} \cos \theta_1 + A^{S_2 L_1} \cos \theta_2) \quad (3)$$

where L_1 denotes the bridge liquid, and the subscripts 1 and 2 refer to the bottom and the top surface, respectively.

Under the experimental conditions of our measurements Eq. (3) can not be directly applied because the effective area does not depend on the volume (or mass) of the liquid but on the separation of the solids, i. e., of the bridge

height. Nevertheless, if one takes also the change in potential energy into account, as was done earlier^{9,10}, direct connection between the critical mechanical instability and change in total energy of the system could be demonstrated.

There is, however, another possibility to analyse the conditions for mechanical stability. We have assumed that the neck-formation, as the first stage of the onset of instability, is the result of capillary waves that are brought about in any cases where fluid interfaces become extremely deformed under dynamic conditions like the detachment of drops from the orifice of a capillary tube. Recent experimental investigations¹⁶⁻¹⁸ have shown that a liquid jet having a periodical meridian profile along its axis is splitted not only in primary drops but also in secondary very small microdroplets. Assuming a sinusoidal shape for the profile, theoretical considerations¹⁹ lead to the result that the critical wave length, at which the jet becomes unstable, is approximately proportional to the square root of the surface or interfacial tension of the fluid surface. Figure 9. shows that this proportionality exists in fact for the diameter of the satellite droplet proving that this way of approach is a reasonable one.

As far as hysteresis is concerned closer consideration of possible changes with separation of the actual geometry reveals that, taking the constant volume condition into account, either the contact angle varies («sticking by hysteresis») or the contact area does or else, what is the general case, both do so. What really happens is dependent upon the energy change which is connected with the actual variation.

The energy needed for the contact circle radius to vary from R_1 to R_2 at a constant contact angle is given by

$$E(R)_\Theta = \Pi (R_2^2 - R_1^2) (\gamma_{SL_2} - \gamma_{SL_1}) = \Pi (R_2^2 - R_1^2) \gamma_{L_1L_2} \cos \Theta \quad (4)$$

The energy connected with the change of the contact angle from Θ_1 to Θ_2 at a constant contact area is the difference of the works of adhesion:

$$E(\Theta)_R = w_2 - w_1 = \Pi R^2 \gamma_{L_1L_2} (\cos \Theta_2 - \cos \Theta_1) \quad (5)$$

The total energy change is clearly the sum of the two energies. If $E(R)_\Theta \gg E(\Theta)_R$ then variation of the contact angle is energetically more favourable, whereas for $E(\Theta)_R \gg E(R)$ the contact area is likely to vary.

In order to prove whether the above treatment can be used to account for actual variations of the configurational changes, contact angle and contact radius values were measured on photographs taken of the menisci of the bridges at different surfactant concentrations with various separation.

The overall picture was found to be rather complicated but some characteristic features are apparent. So, at concentrations less than about 0.2 of the c_M , the contact radius is approximately nonvariant on the polymer surface, and exactly constant on the glass surface as the separation is varied. At higher concentrations it decreases strongly with separation on both surfaces. Contact angles, on the other hand, vary with separation over the whole concentration range according to a minimum curve on PTFE but irregularly fluctuate on glass.

Evaluation of the variation of individual Θ and R data over small displacements of the meniscus near the solid surface showed that the energy conditions as given by Eqs. (4) and (5) are indeed indicative for the direction

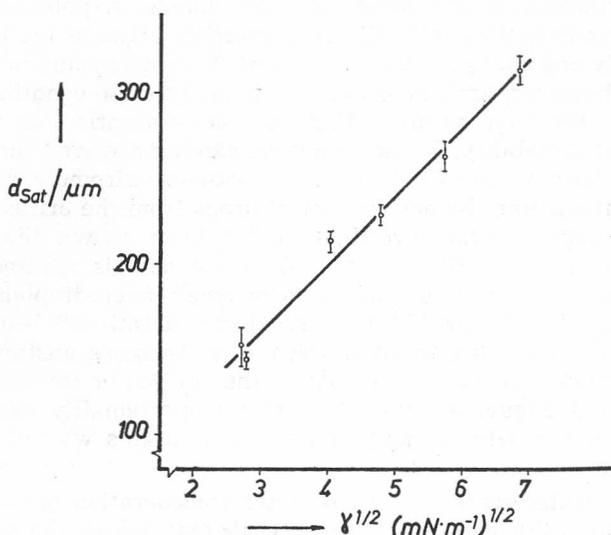


Figure 9. Diameter of the satellite droplet as a function of the square root of the interfacial tension aqueous SDS solution/*n*-octane.

of the actual changes. However, the above treatment is far from being exact due to the lack of detailed knowledge as to the molecular structure within the three-phase boundary region being different from that both in the fluid and solid/liquid interfaces. As is known, the specific state of this »one-dimensional« region manifests itself phenomenologically in the line tension and it is thought that important information will be obtained in future work by taking this parameter into account.

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SAŽETAK

Utjecaj površinski aktivnih tvari na kapilarnu adheziju u četverofaznim sistemima

E. Wolfram i J. Pintér

Svojstva tekućinskog mosta između dodirnih površina dvaju raznorodnih materijala od posebnog su interesa za tehnologiju praškastih materijala i pigmentata, u procesima knjigotiska, za tehnologiju tercijarnog dobivanja nafte iz djelomično iscrpljenih izvora, kao i za pojave kapilarne kondenzacije u poroznim materijalima.

U radu se opisuju istraživanja tekućinskih mostova, koje tvore otopine natrijeva dodecilsulfata između dviju susjednih površina politetrafluoroetilena i stakla. Pokazani su rezultati eksperimentalnog određivanja distribucijskih izoterma te kritičnih parametara veličine kapi za totalnu adheziju. Distribucijske izoterme su po tipu neovisne o koncentraciji površinski aktivne tvari, ali su zato svi kritični parametri za veličinu kapi za totalnu adheziju kao i oni za masu u kapi u stacionarnom stanju jako ovisni o toj koncentraciji. Pojave histereze pri adheziji pripisuju se promjeni kuta kvašenja i/ili promjeni ukupne kontaktne površine. Predložen je konceptualni model i jednadžbe za izračunavanje doprinosa ukupnoj energiji adhezije za ta dva fenomena.

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