

Effect of Surface Expansion and Compression on the Surface Tension of 1-octanol Solutions

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Abstract

This paper investigates how expansion and compression of the surface of a drop containing an organic compound, 1-octanol, affect surface tension. The experiments were performed in a closed chamber where the effect of 1-octanol concentrations in both liquid and gas phases on the surface could be studied. The concentration of 1-octanol varied from 0.2 mM to 2.92 mM (about 70% of its water solubility). Experiments showed surface tension decreased upon compression and increased upon expansion. In expansion when the drop's concentration (at water environment) was greater than 0.5 mM and when the change in surface area of the liquid phase was greater than 5%, the surface tension of the drop exhibited a rapid decrease followed by a gradual increase, back to the "equilibrium" value prior to the expansion. For this case, using Buckingham theorem, a dimensionless parameter was derived and a regression model was fitted to the experimental results of response time delay (the time gap between the change in surface area and the surface tension's response) versus dimensionless parameter. Comparing the dimensionless parameter and the regression model a unique equation $\Delta\gamma = \frac{MC(\Delta S)^{3/2}}{64 \times 10^{-8}}$ was established. Using this equation the surface tension response can be calculated for every molecular weight (M), liquid phase concentration (C), and change in surface area of the liquid phase (ΔS).

Index terms: Adsorption, Buckingham theorem, Compression, Expansion, Surface tension

Introduction

Surface or interfacial tension is widely recognized as one of the most important physiochemical properties of

an interface separating two bulk phases. Studies of surface tension and its influential factors are crucial to the understanding of many natural phenomena and the advancement of numerous technological applications involving a surface or interface. In nature, surface tension can be seen as the driving force that allows insects to glide effortlessly on the surface of still ponds, and a water droplet to bead on the surface of leaves [1], [2]. In environment science, the decrease in surface tension in cloud droplet solutions, due to the dissolved organic compounds from aerosols, has been shown to influence several atmospheric processes such as droplet nucleation, growth, and coalescence [3]. In physiology, the natural pulmonary surfactant, made up of a complex mixture of lipids and proteins, plays a key role in respiration by stabilizing the lungs for proper breathing [4], [5]. More recently, surface tension effects have been used to advance various scientific applications in field such as nano-scale engineering [6]-[8], where surface area-to-volume ratios are large and dominant among material properties.

In many cases, surface tension is highly influenced and even controlled by the presence of a surfactant. In a freshly formed surface, the surfactant is drawn toward the interface to achieve a stable state [9], [10]. The result is a reduction in the surface free energy of the system and therefore a decrease in surface tension [11]. Although adsorption from both liquid and vapor phases should be considered in surface tension behavior, they have been almost always considered exclusive of one another [12], [13]. For example in Langmuir or Frumkin isotherms only adsorption from the liquid phase has been considered [14], [15].

When a volatile surfactant is dissolved in the liquid phase, it also exerts a finite partial pressure in the vapor phase. The question should be asked whether adsorption from both sides of the interface could be considered independent of one another? Dynamic surface tension experiments and model, based on modified Langmuir isotherm, showed that adsorption from both sides of the vapor/liquid interface should be considered simultaneously and the vapor phase plays a key role in this circumstance [16].

For more investigation about the liquid surface structure, in this research the effect of expansion or compression of the surface on the surface tension of an alcohol solution (1-octanol) was measured. In each set of experiments, before any change in the area of the surface, under the effects of vapor pressure and the

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concentration of the drop and environment, the system was allowed to reach to a steady-state (constant surface tension). After the steady-state was attained, the drop was either compressed or expanded, the effect on the surface was investigated through the continuous measurement of surface tension. An interesting effect was observed during some of the expansion experiments (when the drop concentration was greater than 0.5 mM and the change in surface area was greater than 5%) that contradicted with the behavior of conventional surfactants. In such a condition, the surface tension was slightly increased followed by a sharp decrease gradually came back to the value prior to expansion. Also, for predicting the surface tension response to the increase in area of the surface, with respect to the change of the area and the concentration of the drop and environment, Buckingham theorem was used and a dimensionless parameter was established. Using regression analysis, experimental data points were fitted to the dimensionless parameter and a unique equation for predicting the surface tension response was established.

2. Experimental section

2.1. Materials

The chemical 1-octanol, with purity greater than 99%, was purchased from Fluka, Sigma-Aldrich (Oakville, Ontario, Canada). The molecular weight, boiling point, melting point, vapor pressure, vapor density, and specific gravity of 1-octanol are listed in Table I. The water was purified by an ultra-pure water system (Millipore Ltd., Mississauga, Ontario, Canada), with resistivity of 18.2 M Ω . Six different concentrations: 0.2, 0.4, 0.6, 0.8, 1 and 2.92 mM, of 1-octanol were prepared in the water. The sample with highest concentration (about 70% of water solubility of 1-octanol) was prepared as the stock solution and the lower concentrations were made by the dilution of the stock solution. Samples are stored for less than two weeks.

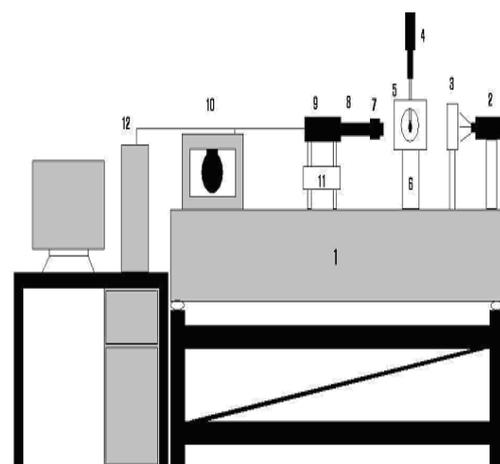
2.2. Surface tension measurement

Different methods have been used to measure surface tension [17], [18]. Axisymmetric Drop Shape Analysis-Profile (ADSA-P) is one of the most accurate methods and has been widely used [19]-[23].

Table 1. The chemical 1-octanol properties

Chemical	1-octanol
Molecular weight (g/mole)	130.23
Boiling point (°C)	195
Melting point(°C)	-16
Vapor pressure at 33°C (mm Hg)	1
Vapor density(g/l)	4.5
Specific gravity (g/cm ³)	0.824

Fig. 1 shows an experimental setup used in our experiments. In this figure, an IsoStation, vibration isolated workstation was used to prevent vibration during surface tension measurements. To illuminate the pendant drop a fiber optic light source filtered by a diffuser was employed. The drop was formed by means of a motorized syringe pump attached to a Hamilton gas-tight syringe. The experiments were performed in a closed chamber (environment chamber) where the effect of 1-octanol concentration in both liquid and gas phases on the surface tension of the drop could be studied. The six different concentrations were used as drop solution concentration as well as environment solution concentration. The tip of the syringe positioned inside a clear quartz cuvette containing environment solution, fixed inside the environment chamber, which allowed control of the vapor phase conditions: temperature and pressure. In order to minimize the vapor leakage during operation, a laboratory parafilm, was used to seal the chamber. The chamber was fixed on a stage that could finely adjust the position of the drop in three directions. The drop images were captured by a high-speed camera and microscope system that displayed the profile on a monochromatic monitor and exported the image files to a computer. An ADSA-P program was used to analyze the images and implement the numerical procedure that yields output results including surface tension, surface area and volume of the drop. Before each set of experiments, the gas-tight syringe was cleaned by Branson B5510 ultrasonic cleaner and repeated rinsing with purified water, THF, and finally dried with pressurized air.



1- Work Station 2- Light Source 3- Diffuser 4- Syringe 5- Environment Chamber 6- Stage 7- Microscope 8- Lens 9- Camera 10- Monitor 11- Stage 12- Computer

Fig. 1. Schematic of an ADSA-P experimental setup

After cleaning the syringe, about 0.3 ml of aqueous solution with specific concentration, as the drop solution, was drawn into the syringe, and 1 ml of the same aqueous solution with different or the same concentration, as the environment solution, was added to the bottom of cuvette and the chamber was sealed. The distance between environment solution and drop was about 1 cm. The system was allowed to equilibrate for 15 minutes. After this time, the drop was formed using a motorized syringe pump. The temperature of the chamber was controlled at 25 °C using a RTE 111 NesLab circulating bath. Image capturing began immediately after the drop was formed and continued with specific interval until the desired time that surface tension reached to a steady-state value.

3. Results and discussion

3-1. Effect of surface area change on dynamic and steady-state surface tension

To further understand the behavior of the interface at the final steady-state condition, several cases of 1-octanol system were subjected to a sudden change in drop volume (surface area) to disrupt the liquid surface structure. Increases of the drop volume and surface area were imparted by an excessive injection of the syringe and making a drop with higher volume and surface area, while when the syringe pull back the drop volume and surface area were decreased. After the experimental “equilibrium” was attained, the pendant drop was either compressed or expanded the effect on the surface structure and adsorption or desorption rates was studied through the continuous measurement of surface tension.

It was observed the surface tension decreased upon compression, while the surface tension increased upon expansion regardless of the concentrations of the drop and the environment solutions (Fig. 2A-C). Figure 2A shows the surface tension response to changes in volume when the drop concentration is higher than the environment concentration. Figure 2B shows the surface tension response to changes in volume when the drop and environment concentrations are equal. Figure 2C shows the surface tension response to changes in volume when the drop concentration is lower than the environment concentration. This is usual behavior of surfactant solutions and can be explained as follows. As the volume is reduced, the concentration of the surfactant per unit area increases, and consequently, the surface tension decreases [14]. As the desorption of the surface surfactant continues, the surface tension gradually comes back almost to the value prior to compression. In the expansion two categories could be happened. If the change in liquid phase volume is less than 8% (or change in surface area is less than 5%) and drop concentration is less than 0.5 mM (category 1), as the surface is expanded

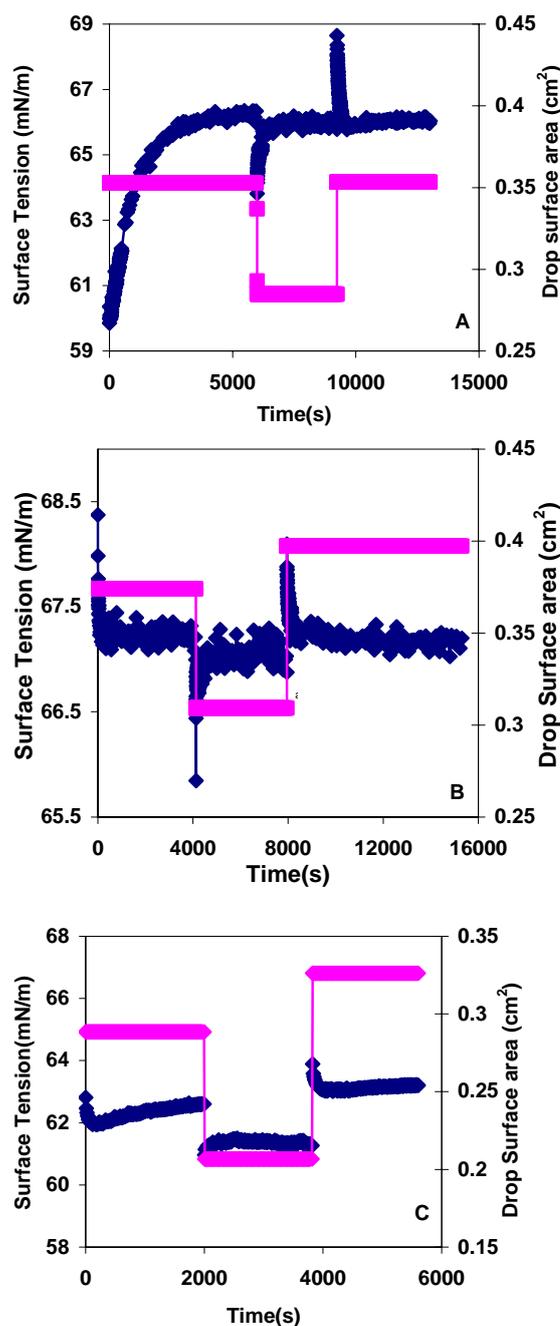


Fig. 2. Effect of changes in surface area on dynamic surface tension of 1-octanol solution. A. The concentration of the drop solution $C_{\text{drop}} = 1 \text{ mM}$ and the concentration of the environment solution $C_{\text{env.}} = 0.2 \text{ mM}$, $C_{\text{drop}} > C_{\text{env.}}$; B. $C_{\text{drop}} = C_{\text{env.}} = 0.4 \text{ mM}$; C. $C_{\text{drop}} = 0.6 \text{ mM}$ and $C_{\text{env.}} = 0.8 \text{ mM}$, $C_{\text{drop}} < C_{\text{env.}}$

the concentration of solute per unit area decreases, and consequently, the surface tension increases. As the adsorption takes place, the surface tension

gradually comes back to the value prior to expansion. An extremely interesting effect was observed in expansion process if the change in liquid phase volume is greater than 8% (or change in surface area is less than 5%) and drop concentration is greater than 0.5 mM (category 2) (Fig. 3,4). These results contradict with the expansion experiments under category 1. In category 2 as the surface area of the drop (drop volume) was increased, the surface tension was slightly increased, but after a certain time (time delay), it was sharply decreased, followed by gradual increase back to the value prior to the expansion (Fig. 3,4). Time delay is a time that after this time surface tension responds to change in surface area (volume). Many runs under category 2 with the same solution, but different concentrations of the drop and environment were performed and the same trend was observed in all of these experiments (Fig. 3,4). This behavior can be explained as follows. As the surface area is expanded, the number of vacant sites at the surface is increased and the surface concentration is decreased. As a result, the surface tension is increased. In the other hand, based on modified Langmuir adsorption isotherms [16]

$$\frac{\Gamma}{\Gamma_{\infty}} = \frac{k_1 p + k_2 c}{1 + k_1 p + k_2 c} \quad (1)$$

if the drop concentration is increased, the adsorption rate will be increased. Thus, in the expansion process, when a fresh drop solution with higher concentration (c) is injected to the former drop, which was in "equilibrium" with the environment with lower concentration [16], the adsorption rate is considerably increased. As a result, the concentration of the surfactant at the surface is increased, and a sharp reduction in the surface tension of the drop can be observed. As the desorption takes place the surface tension gradually comes back to the value prior to expansion (Fig. 3,4).

3-2. Dimensionless parameter

In order to find a meaningful dimensionless parameter to predict the surface tension response to the change of the surface area of the liquid phase in category 2, the Buckingham π theorem was employed. Based on principals of this theorem and the knowledge about the phenomena, the parameters involved in this experiment were chosen as $\Delta\gamma$, Δt , M, C, and ΔS . Where $\Delta\gamma$ (mN/meter) is the amount of sharp decrease in the surface tension after expansion; Δt (sec) is the response time delay; M (gr/mole) is the molecular weight; C (mol/mlit) is the concentration of the surfactant in the drop, and ΔS (cm²) is the change in surface area of the liquid phase. The dimensionless parameter π was defined as follows:

$$\pi = [\Delta\gamma(\Delta t)^2(MC)(\Delta S)^{3/2}] \quad (2)$$

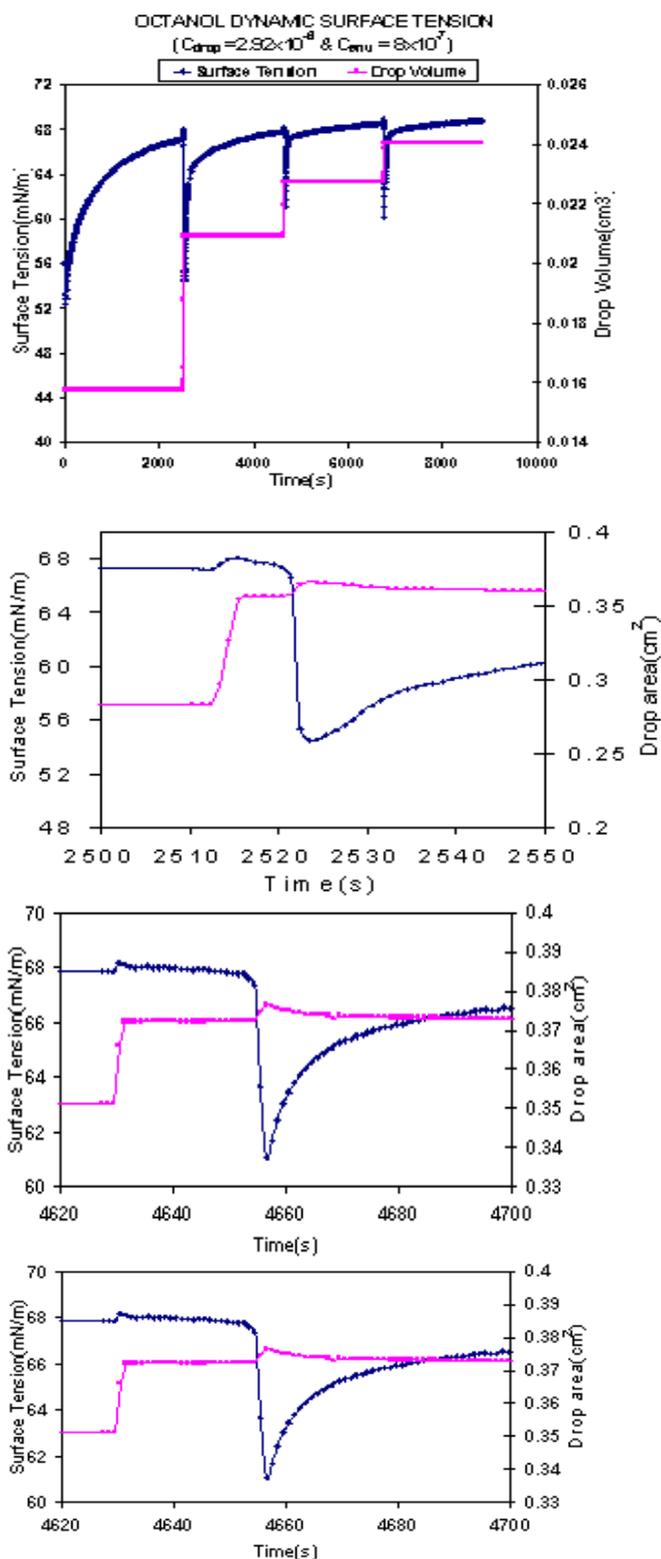


Fig.3. Three sharp decreases of surface tension due to three increases of surface area ($C_{drop} = 2.92 \times 10^{-6}$ mol/mlit & $C_{env} = 8 \times 10^{-7}$ mol/mlit)

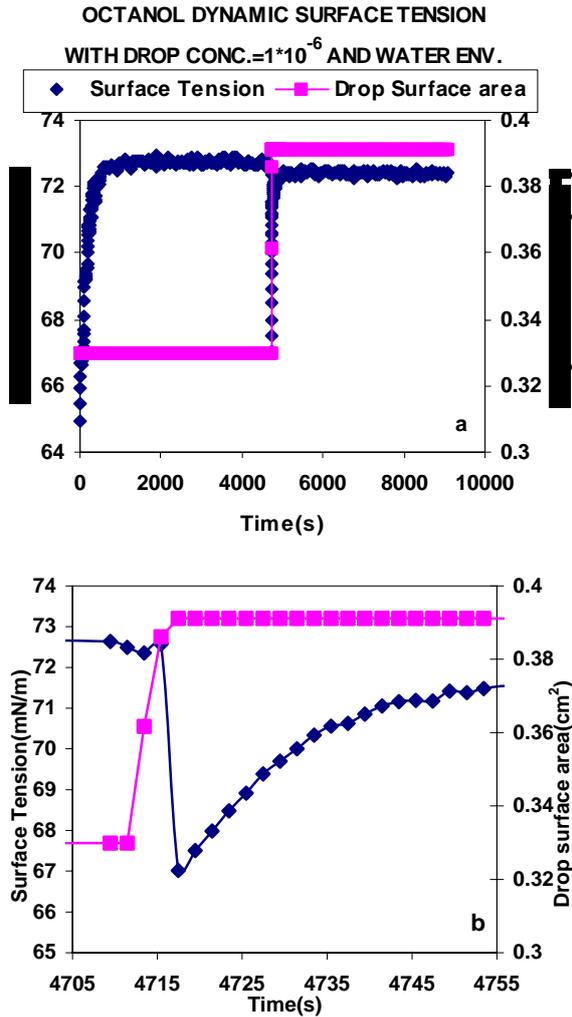


Fig. 4. Sharp decreasing of surface tension due to increase of the surface area when drop concentration is much higher than environment concentration (drop concentration =1.0 × 10⁻⁶ mol/mlt and water environment (Fig. b is the closeup of Fig. a)

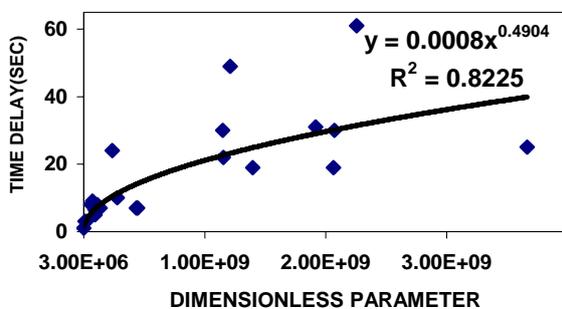


Fig. 5. Response time delay versus dimensionless parameter π

Fig. 5 represents the variation of the response time delay versus dimensionless parameter π . In this figure when the change in volume or the surfactant concentration in the drop increases (lower π value), the response time delay decreases. It can be explained in the following manner. If the change in surface area due to expansion is increased, the number of unoccupied sites in the surface of the drop increases and response time delay for adsorption dynamics should be decreased. Also if the concentration of the solute in the drop is increased, based on modified Langmuir adsorption equation (1), the adsorption rate increases [24]. As a result, the lower the dimensionless parameter π , the lower the response time delay Δt is expected (Fig. 5). Using figure 5, one can predict the response time delay in different drop concentration and different changes in volume. Based on the experimental data, in the best regression model, the time delay has a linear relation with square root of π :

$$\Delta t = K\pi^{0.4904} \cong K\pi^{0.5} \text{ where } K=0.0008\text{sec} \quad (3)$$

The coefficient of determination for this regression model is: $R^2 = 0.8225$

From equation (2):

$$\Delta t = \left(\frac{MC(\Delta S)^{3/2}}{\Delta \gamma} \right)^{1/2} \pi^{1/2} \quad (4)$$

Comparing equation (3) and (4), we can conclude that:

$$K = \left(\frac{MC(\Delta S)^{3/2}}{\Delta \gamma} \right)^{1/2} = 0.0008; \text{ or:}$$

$$K^2 = \left(\frac{MC(\Delta S)^{3/2}}{\Delta \gamma} \right) = 64 \times 10^{-8} \quad (5)$$

Based on equation (5) if the surface tension or the concentration of the drop is changed, the surface tension of the drop is decreased in such a way to satisfy the equation:

$$\Delta \gamma = \frac{MC(\Delta S)^{3/2}}{64 \times 10^{-8}} \quad (6)$$

Using equation (6), in a specific molecular weight, one can predict the surface tension response to the changes of drop concentration and surface area.

Conclusions

- In compression, the surface tension was decreased followed by a gradual increase back to the value prior to compression.
- In expansion when the drop concentration was smaller than 0.5 mM or the changes in liquid phase surface area was smaller than 5% (category 1), the behavior similar to conventional surfactant could be observed. The surface tension was increased followed

by a gradual decrease back to the value prior to expansion.

- In expansion when the drop concentration was greater than 0.5 mM and the change in liquid phase surface area was greater than 5% (category 2), a contradiction between surface tension response for this system and conventional surfactant could be observed. In this system surface tension initially was slightly increased. After a certain time, time delay, it was sharply decreased which was followed by a gradual increase back to the value prior to expansion.

- In expansion under category 2, using π Buckingham theorem, a dimensionless parameter for predicting the surface tension response for the changes of the surface area of liquid phase was derived.

- In expansion under category 2, a regression model for $\Delta\gamma$ versus dimensionless parameter π was fitted to the experimental data. Based on this model, using final equation $\Delta\gamma = \frac{MC(\Delta S)^{3/2}}{64 \times 10^{-8}}$ the surface tension response to the expansion could be predicted.

References

- [1]. Dickinson, M., Animal locomotion: How to walk on water. *Nature*, 2003. 424 (6949): p. 621-622
- [2]. Hu, D.L., B. Chan, and J.W.M. Bush, The hydrodynamics of water strider locomotion. *Nature*, 2003. 424 (6949): p. 663-666.
- [3]. Charlson, R.J., J.H. Seinfeld, A. Nenes, M. Kulmala, A. Laaaksonen, and M.C. Facchini, Atmospheric Science: Reshaping the theory of cloud formation. *Science*, 2001. 292 (5524): p. 2025-2026.
- [4]. Serrano, A.G. and J. Perez-Gil, protein-lipid interactions and surface activity in the pulmonary surfactant system. *Chem. Phys. Lipids*, 2006. 141 (1-2): p. 105-118.
- [5]. Sun Young, P., R.E. Hannemann, and E.I. Franses, Dynamic tension and adsorption behavior of aqueous lung surfactants. *Colloids and surfaces B (Biointerfaces)*, 1999. 15 (3-4): p. 325-338.
- [6]. Vyawahare, S., K.M. Criag, and A. Scherer, Patterning lines by capillary flows. *Nano Lett.* 2006. 6 (2): P. 271-276.
- [7]. Liou, T.M., K.C. Shih, S.W. Chau, and S.C. Chen, Three-dimensional simulations of the droplet formation during the inject printing process. *International communications in heat and mass transfer*, 2002. 29(8): P. 1109-18.
- [8]. Regan, B.C., S. Aloni, K. Jenson, and A. Zettl, Surface-tension-driven nanoelectromechanical relaxation oscillator. *Appl. Phys. Lett.*, 2005. 86 (12): P.123119-1.
- [9]. A.W. Neumann, R.J. Good, R.R. Stromberg (Eds.), *Experimental methods in surface and colloid science*, vol. 11, plenum, New York, 1979, pp. 31-91.
- [10]. Ommelen, J. K., *J. Colloid sci.* 14: 385-400 (1959).
- [11]. Chattoraj, D.K. and K.S. Birdi, *Adsorption and the Gibbs surface excess*. 1ed. 1984, New York, NY: Plenum Press.
- [12]. Hommelen, J.R., The elimination of errors due to evaporation of the solute in the determination of surface tension. *J. Colloid Sci.*, 1959. 14(4): P. 385-400.
- [13]. MacLeoad, C.A. and C.J. Radke, Surfactant exchange kinetics at the air/water interface. *J. Phys. Chem.*, 1985. 89(6): P. 1027-1032.
- [14]. Chang, C.H.; Franses, E.I. *Colloids surf.*, A 1995, 100, 1.
- [15]. Eastoe, J.; Dalton, J.S. *Adv. Colloid interface sci.* 2000, 85, 103.
- [16]. Andrew M. Prpich, M. Elias Biswas, and P. Chen, A new kinetic equation for surfactant transfer. *J. Phys. Chem. C*, 2008, 112(7) PP 2522-2528.
- [17]. J.F. Padday, in: E. Matijevic (ED.), *Surface and colloid science*, Vol. 1, Wiley, New York, 1968, p. 101.
- [18]. J.W. Jennings Jr., N.R. Pallas, *Langmuir* 4 (1988) 959.
- [19]. S. Lahooti, O.I. del Rio, P. Cheng, A.W. Neumann, in: A.W. Neumann, J.K. Spelt (Eds.), *Applied surface thermodynamics*, vol. 1, Marcel Dekker, New York, 1996, p. 441.
- [20]. Neumann, A.W. and J. Spelt, K. *Applied surface thermodynamics. Surfactant science series*. V. 63. 1996, New York, NY: Marcel Dekker, Inc.
- [21]. Fainerman, V. B. & Miller, R., *J. Colloid interface sci.* 178:168 (1996).
- [22]. Rotenberg, Y. & Boruvka, L. and Neumann, A. W., *J. colloid interface sci.*, 93,169 (1983).
- [23]. Del,Rio, O.J. and A.W. Neumann, Axisymmetric drop shape analysis: Computational method for the measurement of interfacial properties from the shape and dimensions of the pendant and sessile drops. *J. Colloid interface sci.*, 1997, 196 (2): p. 136.
- [24]. Adamson, A. W.; Cast, A. P. *Physical chemistry of surfaces*. 6 ed.; Wiley: New York, 1997.