Enhanced and Reversible Contact Angle Modulation of Ionic Liquids in Oil and under AC Electric Field

Shiguo Zhang,[a, b] Xiaodong Hu,[c] Chao Qu,[c] Qinghua Zhang,[a] Xiangyuan Ma,[a] Liujin Lu,[a] Xueli Li,[a] Xiaoping Zhang,[c] and Youquan Deng*[a]

Liquid actuation and manipulation using electrowetting is a rapidly growing field of research and has generated considerable interest in developing technologies such as microfluidic devices, liquid optics and displays.[1] Electrowetting is conventionally carried out with (saline) aqueous solution under DC electric field. However, drawbacks such as evaporation and the inconvenient addition of inorganic salts to enhance the electric conductivity have inevitably limited its application.[2] Therefore, development of new and robust media for electrowetting is highly desirable.

Ionic liquids (ILs), a novel class of versatile solvents and soft materials possessing unique physicochemical properties, including negligible vapor pressure, being liquid over a wide temperature range, intrinsic ionic conductivity and acceptable electrochemistry stability, and so forth,[3] have recently been developed as a promising alternative medium for electrowetting by Millefiorini et al. and other groups.[4] In comparison with saline, IL-based electrowetting systems may be run under some extreme conditions such as in vacuum, or at temperatures either above 373 K or below 273 K.[3c] Recently, studies of electrowetting of ILs in air and under DC electric fields showed some unconventionality compared to saline such as low electrowetting efficiency (contact angle decrease or modulation) and cation/anion-dependent asymmetric behavior,[4] although for the latter there is no unanimity among the different authors.[5] Some effort has also been devoted to the initial applications of electrowetting of ILs as microreactor or microfluidics.[4c, 6] Despite its promising potential, the reported electrowetting of ILs exhibits lower efficiency than that of saline with poor reversibility and a narrow range of contact angle modulation ($< 48°$).

Herein, we presented greatly improved electrowetting efficiency of ILs using oil as the ambient and under AC electric field. Electrowetting behavior of ILs in this case, in particular at a high frequency of 1 kHz, shows greatly enhanced, sensitive, and reversible contact angle modulation in comparison to that in air or under DC electric field.
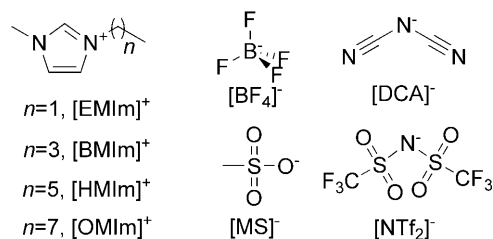

Figure 1. Formulas and structures of the ionic liquids studied.

Seven imidazolium-based ILs with four different anions or four cations of variable alkyl chain length (Figure 1) were selected to investigate the effect of composition and properties of ILs on the electrowetting behavior of ILs. Since the surface tension,[7] the initial contact angle at zero voltage,[4d] and even the electrowetting behavior of ILs[4d] were reported to be sensitive to water content, all ILs were dried in vacuo prior to measurements and the effect of water content on electrowetting of ILs was investigated. An electrowetting device was fabricated on ITO glass first deposited with an insulating parylene N film (CVD, 10 μm, $\varepsilon_r = 2.65$) and then a hydrophobic Teflon AF 1600 film (dip-coating, 900 nm). For further details, see the Supporting Information.

The results of contact angle modulation of ILs in air or dodecane and with DC or AC voltage applied, together with their physical characteristics including surface tension (γ), electrical conductivity (ε), refractive index (n) and viscosity (η), are summarized in Table 1. In air, all ILs exhibit smaller initial contact angles (θ_0, 82–105°), in comparison to that of saline (116°). ILs with lower γ show smaller θ_0, and in particular for [BF$_4$]-based ILs with variable alkyl chain length on cation, a nearly linear relationship between γ and θ_0 can be obtained (Figure S2), which directly confirmed that surface tension values of ILs tend to increase with an increase in hydrophilicity.[8] The liquid–solid interfacial free energy for the air/IL system can be described by the work of adhesion between a liquid and a substrate (W_a), according to the Young–Dupré equation [Eq. (1)]:[9]

$$W_a = \gamma(1 + \cos\theta_0) \tag{1}$$

where stronger interaction between a liquid and a substrate will provide a higher work of adhesion value. According to

[a] Dr. S. Zhang, Q. Zhang, X. Ma, L. Lu, X. Li, Prof. Y. Deng
Centre for Green Chemistry and Catalysis
Lanzhou Institute of Chemical Physics
Chinese Academy of Sciences
Lanzhou, 730000 (China)
Fax: (+86-931-4968116)
E-mail: ydeng@licp.cas.cn

[b] Dr. S. Zhang
Graduate School of Chinese Academy of Sciences
Beijing, 100039 (China)

[c] Dr. X. Hu, C. Qu, Prof. X. Zhang
School of Information Science and Engineering
Lanzhou University, Lanzhou, 730000 (China)

Table 1. Physical characteristics and contact-angle modulation of ionic liquids.[a]

ILs	γ [mN m]	ε [mS cm^{-1}]	η [cP]	W_a [dyne cm^{-1}]	n	Air θ_0	$\Delta\theta_{DC}$[c]	$\Delta\theta_{50}$[d]	$\Delta\theta_{1K}$[d]	Oil θ_0	$\Delta\theta_{DC}$	$\Delta\theta_{50}$	$\Delta\theta_{1K}$
[EMIm][MS]	49.9	2.68[b]	173	37.0	1.4922	105	21	59	65	164	96	116	131
[EMIm][DCA]	47.3	28.00[b]	21	35.9	1.5307	104	21	42	56	166	94	106	129
[EMIm][NTf$_2$]	36.0	9.20[b]	32	41.0	1.4227	82	8	57	51	140	80	101	122
[EMIm][BF$_4$]	49.0	14.00[b]	45	36.3	1.4117	105	30	46	57	165	95	106	137
[BMIm][BF$_4$]	40.6	4.09	140	35.7	1.4155	97	14	67	62	162	106	102	135
[HMIm][BF$_4$]	36.5	1.55	266	37.1	1.4243	89	17	68	62	163	93	120	137
[OMIm][BF$_4$]	31.5	0.75	415	36.4	1.4322	81	15	55	42	159	85	130	126

[a] All measurements conducted at 20 °C, unless otherwise indicated. [b] Data at 25 °C. [c] Modulation range of contact angle (deg.) before saturation for the positive side. [d] Modulation range of contact angle (deg.) between 0 V and 250 V.

Table 1, W_a values of ILs with same [EMIm]$^+$ cation decrease in the order of [NTf$_2$]$^-$ > [MS]$^-$ ~ [BF$_4$]$^-$ ~ [DCA]$^-$, while for ILs with same [BF$_4$]$^-$ anion, no obvious change in their W_a values was observed. It appears that for all ILs investigated, W_a values are anion-dependent and larger anions have stronger interactions with Teflon layer than smaller anions. Among all anions, [NTf$_2$]$^-$ have the largest volume while the other three anion have comparable and small volume. This order is similar to that of the W_a values, however, opposite to the case of [BMIm]$^+$-based ILs.[4d] The reason for this is unclear.

When a DC electric field is applied, the saturated contact angle (θ_s) is around 80° for all ILs and the resulted change in the contact angle ($\Delta\theta$) is no more than 30°. Under the same conditions, however, the AC electric field enhances the ultimate wettability (indicated by θ at high voltage ~250 V) of the ILs and thus the modulation range (42–67°). To further increase the modulation range and considering that most electrowetting and applications, such as display and variable-focus liquid lenses, are performed in oil,[1a, 10] dodecane was used instead of air to give rise to high θ_0 for potential wide modulation. As expected, the θ_0 of the ILs increased significantly and all θ_0 are around 160° (except [EMIm][NTf$_2$], $\theta_0 = 140°$), which could be attributed to the substantial decrease of interfacial tension involving liquid/air and solid/air to liquid/oil and solid/oil, respectively, according to Young's equation. Despite the much higher θ_0 in oil than in air, the ultimate wettability is not depressed but enhanced, irrespective of the case under DC or AC voltage. Thus the modulation range is noticeably widened, as shown in Table 1. Moreover, the electrowetting efficiency in oil is improved in the order of DC (80–106°) < 50 Hz (101–130°) < 1 kHz (122–137°), which is similar to that in air. A typical contrast modulation of [EMIm][BF$_4$] in air or oil and under DC or AC electric fields is illustrated in Figure 2.
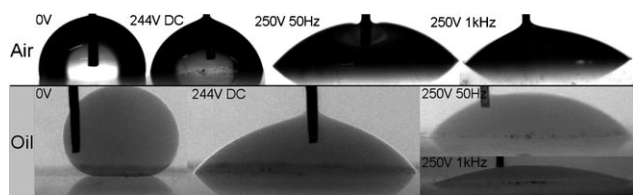

Figure 2. Contact angle modulation (0 V and 250 V) of [EMIm][BF$_4$] in air or dodecane and with DC or AC voltage applied.

The electrowetting behavior of [EMIm][NTf$_2$] is given in Figure 3 as a typical example. Under DC voltage, the electrowetting behavior of [EMIm][NTf$_2$] is generally similar to the
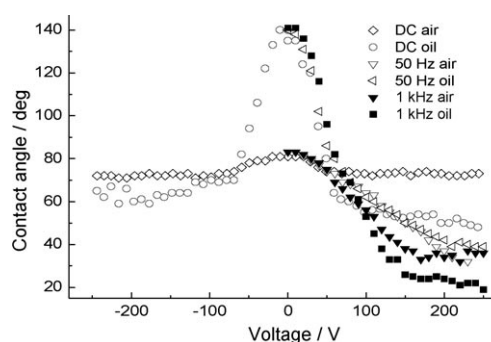

Figure 3. Electrowetting curves of [EMIm][NTf$_2$] in air or dodecane and with DC or AC voltage applied (only comparison between AC and positive DC curves are given for clarity).

electrowetting curves for ILs on poly(tetrafluoroethylene) film in air.[5] The variation of the contact angle with the applied external voltage, V, can be readily described by the Young–Lippmann equation [Eq. (2)]:

$$\cos\theta = \cos\theta_0 + (\varepsilon_r\varepsilon_0/2\gamma d)V^2 = \cos\theta_0 + bV^2 \qquad (2)$$

which is valid below a certain voltage (69 and −69 V), indicating nearly ideal electrowetting at low voltages (values of the free parameters, $\cos\theta_0$ and b are given in Table S1 in the Supporting Information). Note that for all ILs, there is slight asymmetry for the fitted electrowetting curve (before saturation), where the negative contact angles are higher than the theoretic values but the positive ones are less (Figure S7, Supporting Information). Such an asymmetry in the electrowetting curve is similar but slightly weak in comparison with the IL polymer as reported by Laskoski et al.,[4b] which had small cationic molecules in a large anionic polyelectrolyte. Such an asymmetry in the electrowetting curve was suggested to originate from the anion–cation asymmetry of the ILs.

Although the contact angle modulation of [EMIm][NTf$_2$] in oil and under DC electric field is nearly ten times wider to

that in air (8°), up to 80°, a 50 Hz AC electric field was further applied in oil, since AC elctrowetting can facilitate wide modulation in air. The saturated contact angle is drastically delayed from 90 V under DC electric field to 210 V under 50 Hz AC electric field, with a modulation range as high as 101°. However, the IL droplets showed slight oscillation under this low frequency, especially for low-viscosity ILs at a voltage around 100 V, due to their relatively low mechanical eigenfrequency (depending on the viscosity) close to the frequency of the applied voltage.[11] In contrast, ILs droplets under high frequency (1 KHz) showed not only a steady shape, but also further improved electrowetting efficiency, which is in good agreement with the result obtained by Nanayakkara et al.[12] As shown in Figure 3, the ultimate wettability of [EMIm][NTf$_2$] is improved (24°) although there is a slight decrease in the saturated voltage from 210 V at 50 Hz to 180 V at 1 KHz. The AC electrowetting at 50 or 1 KHz is close to DC below a certain voltage (for [EMIm][NTf$_2$], ca. 70 V), while saturated at certain higher voltage. The saturation occurring here appears to be the instability of the contact line because the IL droplet becomes unstable and emits small satellite droplets (Figure S8, Supporting Information),[2a] in particular for less conductive ILs.

The application of an AC electric field as a function of the type of cation and anion exhibits a remarkable change in the wetting behavior of ILs. As for [EMIm]$^+$-based ILs (Supporting Information, Figure S9, left), although no significant difference in electrowetting behavior (θ_0, θ_s, and even electrowetting curves) occur upon changing the anions, [EMIm][NTf$_2$] have lower θ_0 and improved ultimate wettability, due to its low surface tension. In contrast, saline showed ultimate wettability as high as 52°, for which the modulation range (116°) is obviously narrower than all the ILs investigated. While for the [BF$_4$]$^-$-based imidazolium ILs with increasing alkyl chain length on cation (Supporting Information, Figure S9, right), [OMIm][BF$_4$] required a lower voltage to spread over the hydrophobic surface. The fitted values of the free parameters, $\cos \theta_0$ and b nearly changed with the order of their surface tensions (Figure 4 and Table 2). Hence, our electrowetting results demonstrate that ILs with long alkyl chain could be better choice to enhance the surface hydrophilicity.
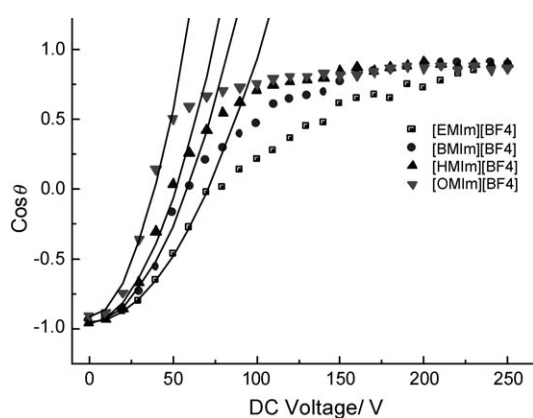

Figure 4. Electrowetting curves of four [BF$_4$]$^-$-based ILs in oil and under 1k Hz AC electric field. The solid lines are fits of the Young–Lippmann equation.

Table 2. Fitted values of the free parameters, $\cos \theta_0$ and b for the four [BF$_4$]-based ILs investigated.

ILs	$\cos \theta_0$	b
[EMIm][BF$_4$]	−0.95769	0.00019
[BMIm][BF$_4$]	−0.96068	0.00028
[HMIm][BF$_4$]	−0.96185	0.00036
[OMIm][BF$_4$]	−0.92132	0.00060

High reversibility for all IL droplets was observed in dodecane and under AC voltage. For example, [EMIm][BF$_4$] exhibits good reversibility, particularly at high voltage (>100 V, see Figure S10, Supporting Information), while below 100 V its hysteresis is up to 10°. This is consistent with reports that oil impregnation reduces the contact angle hysteresis of Teflon AF films.[2b, 13] The sensitivity of contact angle vs voltage is also enhanced in oil. The threshold voltage required to actuate ILs droplets in air is generally higher than 30 V. However, obvious change is found as low as 10 V in oil.

In order to investigate the effect of water content on electrowetting of ILs, experiments in oil and under a 1 kHz AC electric field was conducted for a typical hydrophobic ILs ([EMIm]-[NTf$_2$] and water-saturated [EMIm][NTf$_2$]) and a typical hydrophilic ILs ([EMIm][BF$_4$] and its diluted solutions). The effect of water content on electrowetting of ILs was found to be profound for hydrophilic ILs, but smaller for water-saturated hydrophobic ILs (Supporting Information, Figures S11, S12). Especially at high voltages (>100 V), relatively large deviations were observed. However, the effect of water was smaller for water-saturated hydrophobic ILs—almost the same electrowetting curves were observed. The different effect of water content on electrowetting of hydrophilic and hydrophobic ILs was similar to the reported cases in air and under DC electric field.[4d]

Relaxation behavior of reversible electrowetting for all ILs in oil was investigated (Supporting Information, Figure S13). At 50 Hz and once voltage (200 V) applied, both the time for spreading of the droplet and for recovery upon removal of electrical potential are viscosity dependent. For low-viscosity ILs ([EMIm][DCA], [EMIm][NTf$_2$], and [EMIm][BF$_4$]), both the time for spreading and recovery are less than 2 s. While for high-viscosity ILs ([HMIm][BF$_4$] and [OMIm][BF$_4$]), the spreading time is even up to 5–8 s, while the retracting time is less than 3 s. For most ILs, increasing the frequency to 1 KHz slightly delayed the spreading while accelerating the recovery of the ILs droplet.

The results show that the contact angle change in three different systems decreased in the order [V$_{AC}$/oil] > [V$_{AC}$/air] > [V$_{DC}$/air]. The higher contact angle change with AC conditions is mainly due to the "RC filter effect". The experiment setup of electrowetting can be compared to a RC filter circuit (as shown in the Supporting Information, Figure S14).[12,14] The values of the equivalent resistors (R_i) and capacitors (C_i) of the ILs droplet are both functions of the contact angle (θ) because of the spherical cap geometry of the droplet and the voltage-induced contact angle reduction.[14] For the insulator layer (parylene

and Teflon), its equivalent resistors (R_d) and capacitors (C_d) are also both functions of contact angle (θ) because the cross section area A is changed with contact angle (θ). Thus the voltage loss across the insulator layer [V, part of the total voltage (V_o), and which induces contact angle change according the Young–Lippmann equation], calculated by using the impedance of the ILs and dielectric layers, is correlated to the frequency (f) of the applied AC electric field and contact angle (θ), that is, for a given IL in AC conditions, contact angle is a function of both frequency and voltage. According to the previous reports,[12,14b] the critical frequency of RC-low-pass filter for the droplet can be written as Equation (3):

$$f_c = F(R_i, C_i, R_d, C_d) \tag{3}$$

When $f \gg f_c$, that is, at high frequencies, the liquid is purely insulating. When $f \ll f_c$, that is, at low frequencies, the liquid behaves as a pure conductor. For electrowetting of saline droplet in this case (at high frequencies), increasing the frequency lead to little change in the contact angle.[14a,d] In our work, increasing the frequency from 50 to 1 kHz further resulted in wide modulation of contact angle, which is similar to the result as obtained by Jones et al,[14c] in which the height-of-rise of DI water is frequency dependent and increased from DC to 1 kHz. Both cases could be related to the critical frequency of ILs and DI water, respectively. However, in a DC electric field, the capacitors (C_i) of the IL droplet can be neglected and V is equal to V_o, thus the contact angle is a function of only voltage in the DC case. However, the smaller contact angle modulation in DC case can be correlated to contact angle saturation because of charge-induced permanent ion adsorption on the substrate, while in the AC case it is reduced by the time-variable changed polarity. When the ambient is changed from air to oil, the wider modulation than air is due to three reasons. First, the initial contact angle (θ_0) is greatly increased due to the substantial decrease of interfacial tension involving liquid–vapor surface tension (γ_{lv}) and solid–vapor surface tension (γ_{sv}) to liquid–oil interface tension (γ_{lo}) and solid–oil interface tension (γ_{so}), which offers a possibility for potential wide modulation. Second, the liquid–vapor surface tension (γ_{lv}) in the Young–Lippmann equation decreases to liquid–oil interface tension (γ_{lo}), indicating that under identical conditions, oil ambient offers a wide change. Third, the RC filter circuit can be explained using a similar model as reported by Chatterjee et al.,[14b] extra capacitance and resistor value will be added to the system due to the oil instead of air, which may result in the decrease of voltage loss across the insulator layer.

In conclusion, as compared to that in air or under a DC electric field, electrowetting of ILs in dodecane and under AC electric field shows attractive features involving wide modulation of the contact angle, delay of the contact angle saturation, decrease in contact angle hysteresis, and an increase in sensitivity. In particular at the high frequency of 1 kHz, stable, reversible and wide-contact-angle modulation (122–137°) was obtained. The efficiency could be further improved through optimal choice of ambient phase or rational design of ILs. The wide modulation corroborated the potential of ILs to be sub-stantial media for electrowetting-based liquid actuation, particularly in some extreme conditions or in practical applications (generally conducted at 1 K Hz oil ambient), such as variable-focus ionic-liquid lenses.

Experimental Section

An insulating layer of Parylene N was deposited on an ITO-coated (ITO: indium-tin-oxide) glass substrate by chemical vapor deposition (10 μm, $\varepsilon_r = 2.65$). Subsequently a thin hydrophobic layer top coating was deposited by dip-coating as follows: the insulating layer was immersed in a 4% (w/v) of Teflon AF 1600 (DuPont) in FC 75. The substrate was withdrawn from the solution at a constant speed of 750 μm s^{-1} and the procedure was repeated twice. The resulting Teflon-covered ITO glass slides were heat-treated for 6 min at 112 °C, and for 5 min at 165 °C, in order to remove residual solvent and improve the adhesion of the Teflon layer to the substrate, which needs a thin Teflon coating (0.9 μm, $\varepsilon_r = 1.93$) as a top layer to obtain the desired hydrophobic and low hysteresis properties. An AC electrical signal is supplied by a function generator with frequency varying from 50 to 1k Hz and applied voltage up to 250 V in root-mean-square (rms) value. All voltages in this paper are rms values. Typically, an ILs droplet (3 μL) was placed on the substrate located in a groove through a syringe. A thin Pt wire (150 μm in diameter) was inserted into the droplet as a working electrode. Then dodecane was transferred into the groove with a pipette immediately in order to reduce moisture. Electrowetting behavior was measured by step-wise increase in the applied voltage and by capturing the image of the droplet after each voltage step. Each experiment was conducted on a fresh area of surface and used a fresh droplet to avoid effects associated with residual charging. For ILs with refractive index close to that of dodecane ($n = 1.4168$), visibility and contrast were improved by adding a trace amount of dye (Rhodamine 6G) to the liquid for discrimination. The reversibility was tested by first increasing voltage from 0 to 250 V then decreasing the voltage form the maxima value to 0 V, with both steps of 10 V.

[1] a) F. Mugele, J. C. Baret, *J. Phys. Condens. Matter* **2005**, *17*, R705–R774; b) R. A. Hayes, B. J. Feenstra, *Nature* **2003**, *425*, 383–385.

[2] a) F. Mugele, A. Klingner, J. Buehrle, D. Steinhauser, S. Herminghaus, *J. Phys. Condens. Matter* **2005**, *17*, S559–S576; b) M. S. Dhindsa, N. R. Smith, J. Heikenfeld, P. D. Rack, J. D. Fowlkes, M. J. Doktycz, A. V. Melechko, M. L. Simpson, *Langmuir* **2006**, *22*, 9030–9034; c) N. Verplanck, E. Galopin, J. C. Camart, V. Thomy, Y. Coffinier, R. Boukherroub, *Nano Lett.* **2007**, *7*, 813–817.

[3] a) M. J. Earle, K. R. Seddon, *Pure Appl. Chem.* **2000**, *72*, 1391–1398; b) J. H. Davis, Jr., P. A. Fox, *Chem. Commun.* **2003**, 1209–1212; c) *Ionic Liquids in Synthesis* (Eds.: P. Wasserscheid, T. Welton), Wiley-VCH, Weinheim, **2003**.

[4] a) S. Millefiorini, A. H. Tkaczyk, R. Sedev, J. Efthimiadis, J. Ralston, *J. Am. Chem. Soc.* **2006**, *128*, 3098–3101; b) H. L. Ricks-Laskoski, A. W. Snow, *J. Am. Chem. Soc.* **2006**, *128*, 12402–12403; c) D. Chatterjee, B. Hetayothin, A. R. Wheeler, D. J. King, R. L. Garrell, *Lab Chip* **2006**, *6*, 199–206;

d) Y. S. Nanayakkara, H. Moon, T. Payagala, A. B. Wijeratne, J. A. Crank, P. S. Sharma, D. W. Armstrong, *Anal. Chem.* **2008**, *80*, 7690–7698.

[5] J. Restolho, J. L. Mata, B. Saramago, *J. Phys. Chem. C* **2009**, *113*, 9321–9327.

[6] a) W. Wang, R. W . Murray, *Anal. Chem.* **2007**, *79*, 1213–1220; b) P. Dubois, G. Marchand, Y. Fouillet, J. Berthier, T. Douki, F. Hassine, S. Gmouh, M. Vaultier, *Anal. Chem.* **2006**, *78*, 4909–4917; c) P. Dubois, G. Marchand, S. Gmouh, M. Vaultier, *Chem. Eur. J.* **2007**, *13*, 5642–5648.

[7] W. W. Liu, T. Y. Zhao, Y. M. Zhang, H. P. Wang, M. F. Yu, *J. Solution Chem.* **2006**, *35*, 1337–1346.

[8] a) E. Wanigasekara, X. T. Zhang, Y. Nanayakkara, T. Payagala, H. Moon, D. W. Armstrong, *ACS Appl. Mater. Interfac.* **2009**, *1*, 2126–2133; b) Y. P. Zhu, M. J. Rosen, S. W. Morrall, *J. Surfactants Deterg.* **1998**, *1*, 1–9.

[9] J. N. Israelachvili, *Intermolecular and Surface Forces*, 2nd ed., Academic Press, London **1991**.

[10] S. Kuiper, B. H. W. Hendriks, *Appl. Phys. Lett.* **2004**, *85*, 1128–1130.

[11] J. M. Oh, S. H. Ko, K. H. Kang, *Langmuir* **2008**, *24*, 8379–8386.

[12] Y. S. Nanayakkara, S. Perera, S. Bindiganavale, E. Wanigasekara, H. Moon, D. W. Armstrong, *Anal. Chem.* **2010**, *82*, 3146–3154.

[13] a) H. J. J. Verheijen, M. W. J. Prins, *Langmuir* **1999**, *15*, 6616–6620; b) M. G. Pollack, A. D. Shenderov, R. B. Fair, *Lab Chip* **2002**, *2*, 96–101.

[14] a) A. Kumar, M. Pluntke, B. Cross, J. C. Baret, F. Mugele, *Proceedings of the Materials Research Society Fall Meeting*, Boston, November, **2005**, E-N06–01.1; b) D. Chatterjee, H. Shepherd, R. L. Garrell, *Lab Chip* **2009**, *9*, 1219–1229; c) T. B. Jones, K. L. Wang, *Langmuir* **2004**, *20*, 2813–2818; d) J. Hong, S. Ko, K. Kang, I. Kang, *Microfluid. Nanofluid.* **2008**, *5*, 263–271.