

Ionic Liquids Are Useful Contact Angle Probe Fluids

Lichao Gao and Thomas J. McCarthy*

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003

Received January 9, 2007; E-mail: tmccarthy@polysci.umass.edu

Measuring the contact angles that probe fluids make with solid surfaces is a standard and widely used analytical technique for characterizing the surface properties of solids.^{1,2} Water is the most widely used probe fluid, but dozens of other liquids have been used.^{3–6} Liquids of varying surface tension can determine critical surface tensions of solids,^{3–5} aqueous solutions of varying pH can derive acidity coefficients of surfaces,^{7,8} and probe fluids of varying molecular volume can determine the dimensions of nanopores in monolayers.⁶ Subtle changes in functional group orientation can be detected.^{9,10} Hysteresis (the difference between advancing (θ_A) and receding (θ_R) angles) yields information on the structure of the three-phase contact line.^{11–15} The relative roughness¹⁶ of surfaces and the composition of composite surfaces¹⁷ can be estimated by contact angle.

Ionic liquids have received increasing attention due to their unique characteristics as solvents:^{18–21} low vapor pressure, wide use temperature ranges, thermal stability, nonflammability, ionic conductivity. These liquids are primarily derived from organic cations and noncoordinating anions that together form salts with weak interionic interactions that lower melting points to near room temperature. The literature before mid-2006 on the use of ionic liquids for polymer synthesis, processing, and application has been reviewed.²⁰ This field is described in this review as “at an early stage of development.” Here we address the use of ionic liquids as contact angle probe fluids. There are three very recent reports of contact angles of ionic liquids, but none of this research was directed at surface analysis. Two different types of Teflon were studied. Static contact angles of three ionic liquids on Teflon AF (a random copolymer of tetrafluoroethylene and perfluoro-2,2-dimethyl-1,3-dioxol-4-ene) were measured²² as part of a study on electrowetting of ionic liquids. The solvation by four ionic liquids of surface functionality on controlled porosity glass was studied by fluorescence spectroscopy.²³ These authors state that “there is little information on how ionic liquids solvate/wet molecules attached to surfaces” and give no references to this subject. They report apparently advancing contact angles of four ionic liquids on Teflon (poly(tetrafluoroethylene)) which were used to estimate surface tension values for these liquids. In a report of using ionic liquid droplets as microreactors, static contact angles of seven ionic liquids on Teflon AF were reported.²⁴

Figure 1 shows structures of the ionic liquids studied in the work reported here. We chose these liquids as examples of those that should exhibit high surface tension so that we could compare the contact angles with those of water on several hydrophobic surfaces that we are currently studying. The surface tension of $C_5H_9N_2^+CH_3SO_4^-$ over a 20 °C temperature range has been reported²⁵ as 58.9–60.9 dyn/cm. Surface tensions of longer *n*-alkyl chain-containing methylimidazolium salts have been measured.^{26,27} The values vary from ~43 (for *n*-butyl) to ~24 dyn/cm (for *n*-dodecyl), and also vary as a function of the anion structure. There are discrepancies between these two reports.

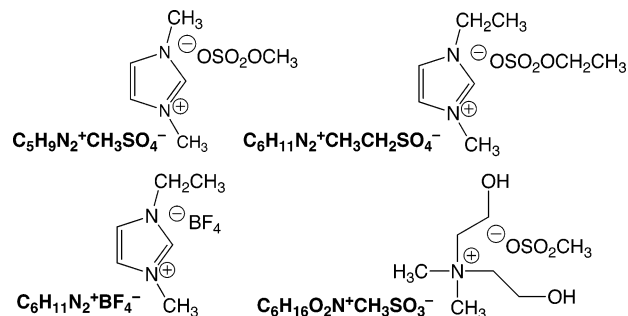


Figure 1. Structures and formulas for the ionic liquids studied.

Table 1 shows advancing and receding contact angle values (reported as θ_A/θ_R) for water and four ionic liquids on seven different surfaces. The last row (entry 8) lists surface tensions for these liquids that we measured using a pendant drop method.²⁸ The values should be considered accurate in terms of the probe fluid used for contact angle analysis but not accurate values for the pure substances; no effort was made to purify the liquids, and they most certainly contained water, as we handled them in air. The first four entries (rows) in the table are superhydrophobic surfaces. OTFE is a compressed sample of a commercial²⁹ lubricant that we have reported³⁰ exhibits water contact angles of $\theta_A/\theta_R = 177^\circ/177^\circ$. $SiPFA^{Posts}$ is a silicon wafer that was patterned by photolithography to contain staggered rhombus posts and modified using hepta-decafluoro(1,1,2,2-tetrahydro)decyldimethylchlorosilane. We have reported³¹ water contact angles of $\theta_A/\theta_R = 168^\circ/153^\circ$ for this surface. $SiMeSiCl_3$ is a silicon wafer that was treated with $MeSiCl_3$ in toluene in the presence of humidified air. The preparation of this surface has been reported as were water contact angles of $\theta_A/\theta_R = 175–178^\circ/180^\circ$.¹² $SiMe_3SiCl/SiCl_4$ is a silicon wafer that was treated with an azeotropic mixture of Me_3SiCl and $SiCl_4$ in the gas phase at room temperature and 45% relative humidity.³² Entries 5–7 in Table 1 are smooth surfaces of the covalently attached perfluoroalkyl monolayer described above ($SiPFA$),³¹ a covalently attached dimethylsiloxane oligolayer of ~2.5 nm thickness ($SiMe_2SiCl_2$),³³ and a commercial polyester film sample that we have studied (PET).³⁴

The data in Table 1 warrant discussion, and we do so in the next paragraph but point out that there is an absence of useful literature that can be used for comparison and note the potential complexity of contact angle analysis using ionic liquids. We believe that this complexity will eventually be viewed as versatility and will make ionic liquids lucid probe fluids. Either ion of the probe liquid could have specific interactions with a surface that could be studied by varying the counterion. In studying solvent–solute interactions in ionic liquids, some researchers suggest³⁵ that the solvent should be treated as a binary mixture and the solution as a ternary mixture. The same should be the case for ionic liquid–surface interactions: the ionic volume of both ions should affect contact angle results for surfaces with nanoscopic topography. These

Table 1. Advancing and Receding Contact Angles (θ_A/θ_R) of Water and Ionic Liquids on Various Hydrophobic Surfaces

entry	surface	H ₂ O	C ₅ H ₉ N ₂ ⁺ CH ₃ SO ₄ ⁻	C ₆ H ₁₁ N ₂ ⁺ C ₂ H ₅ SO ₄ ⁻	C ₆ H ₁₁ N ₂ ⁺ BF ₄ ⁻	C ₁₆ H ₁₆ O ₂ N ⁺ CH ₃ SO ₃ ⁻
1	OTFE	178°/178°	175°/175°	>175°/>175°	177°/175°	>175°/>175°
2	SiPFA ^{Posts}	169°/151°	170°/148°	174°/150°	172°/149°	174°/153°
3	SiMeSiCl ₃	177°/176°	175°/~10°	126°/9°	122°/9°	174°/<8°
4	SiMe ₃ SiCl/SiCl ₄	176°/172°	170°/~10°	126°/~10°	130°/17°	118°/8°
5	SiPFA	117°/109°	101°/91°	97°/86°	95°/83°	100°/85°
6	SiMe ₂ SiCl ₂	104°/102°	95°/91°	91°/80°	83°/82°	95°/93°
7	PET	82°/49°	65°/34°	61°/32°	59°/32°	69°/42°
8	γ_{LV} (dyn/cm)	72.3	64.2	49.4	49.2	66.4

volumes vary significantly in ionic liquids;¹⁸ for instance, the volumes of BF₄⁻ and ⁻N(SO₂CF₃)₂ (many ionic liquids are available with these anions) are 0.073 and 0.232 nm³. Dipole–dipole, charge–charge, and charge–dipole interactions between surfaces and ionic liquids should also be important. Charge density/charge dispersity and dipole density/dipole strength at the liquid–solid interface will be affected by (and controllable with choice of) the ionic liquid molecular volume.

Entries 5–7 in Table 1 show contact angle data for three smooth surfaces: a silicone surface, a perfluoroalkyl surface, and a polyester surface. Contact angles for these surfaces are lower than those of water and in line with the surface tension data. The lower surface tension liquids, C₆H₁₁N₂⁺C₂H₅SO₄⁻ and C₆H₁₁N₂⁺BF₄⁻, exhibit lower contact angles than the higher surface tension liquids, C₅H₉N₂⁺CH₃SO₄⁻ and C₆H₁₆O₂N⁺CH₃SO₃⁻. We note that the low hysteresis (~2° as assessed by water) surface, SiMe₂SiCl₂, exhibits low hysteresis (1–4°) for three of the four ionic liquids but significant hysteresis (11°) for the other. Entries 1 and 2 show data for contact angles on rough perfluoroalkyl surfaces. OTFE has binary length scale topography, consisting of multimicron disordered hills, valleys, and crevices of submicron spherical particles of tetrafluoroethylene oligomers.^{29,30} SiPFA^{Posts} is a Si surface with staggered rhombus-shaped posts, the diagonals and height of which are 4, 8, and 40 μm, respectively.³¹ The contact angles of all of the ionic liquids are very high and indistinguishable from those of water. This is a surprising result that is not in concert with surface tension. Contact angles of this magnitude for liquids other than water have not been reported. The contact angles for methylene iodide on OTFE ($\theta_A/\theta_R = 140°/138°$)³⁰ are significantly lower than these values, although its surface tension ($\gamma_{LV} = 50.8$ dyn/cm)⁵ is higher than that of C₆H₁₁N₂⁺C₂H₅SO₄⁻ and C₆H₁₁N₂⁺BF₄⁻. Entries 3 and 4 in Table 1 are for superhydrophobic methylsilicone surfaces.^{12,32} The near-perfect hydrophobicity is due to their contorted fibrillar topography. These two surfaces, SiMeSiCl₃ and SiMe₃SiCl/SiCl₄, exhibit high, but variably high advancing contact angles and very low receding contact angles with all four ionic liquids. These results indicate significant wettability differences between the silicone and perfluoroalkyl surfaces that are not discernible from the water contact angle data. Both perfluoroalkyl surfaces exhibit Cassie behavior;¹⁷ water and the ionic liquids rest on top of surface asperities. The two silicone surfaces show Cassie behavior with water but Wenzel behavior¹⁶ with ionic liquids. The ionic liquids penetrate the fibrillar topographic features and exhibit low receding contact angles. The marked difference in contact angle hysteresis between the perfluoroalkyl and silicone surfaces emphasizes that both advancing and receding contact angles are required to adequately characterize a surface.

In summary, we report the use of ionic liquids for contact angle analysis of surfaces. Smooth surfaces of various chemical composition exhibit contact angles with ionic liquids that are lower than values obtained with water and that scale with liquid surface tension values. Contact angles of ionic liquids on rough perfluoroalkyl

surfaces exhibit high contact angles that are indistinguishable from those of water and not dependent on liquid surface tension. Superhydrophobic methylsilicone surfaces that exhibit high water contact angles and low hysteresis exhibit very low receding contact angles with ionic liquid probe fluids and high hysteresis. We believe that, because of their variable and controllable surface tension, interface charge density, interface dipole density, as well as their variable and controllable cation/anion structure and molecular volume, ionic liquids are useful contact angle probe fluids.

Acknowledgment. We thank the NSF-sponsored MRSEC and RSEC centers at the University of Massachusetts for financial support, and Drs. Joachim Venzmer and Peter Schwab of Degussa for discussion and ionic liquid samples.

References

- (1) Mittal, K. L. *Contact Angle, Wettability and Adhesion*; VSP: Utrecht, The Netherlands, 1993.
- (2) Sun, T.; Feng, L.; Gao, X.; Jiang, L. *Acc. Chem. Res.* **2005**, *38*, 644–652.
- (3) Shafirin, E. G.; Zisman, W. A. *J. Phys. Chem.* **1960**, *64*, 519–524.
- (4) Zisman, W. A. *Adv. Chem. Ser.* **1963**, *43*, 1–51.
- (5) Shafirin, E. G.; Zisman, W. A. *Adv. Chem. Ser.* **1963**, *43*, 145–157.
- (6) Fadeev, A. Y.; McCarthy, T. J. *Langmuir* **1999**, *15*, 7238–7243.
- (7) Holmes-Farley, S. R.; Reamey, R. H.; McCarthy, T. J.; Deutch, J.; Whitesides, G. M. *Langmuir* **1985**, *1*, 725–740.
- (8) Shoichet, M. S.; McCarthy, T. J. *Macromolecules* **1991**, *24*, 982–986.
- (9) Cross, E. M.; McCarthy, T. J. *Macromolecules* **1990**, *23*, 3916–3922.
- (10) Gagnon, D. R.; McCarthy, T. J. *J. Appl. Polym. Sci.* **1984**, *29*, 4335–4340.
- (11) Gao, L.; McCarthy, T. J. *Langmuir* **2006**, *22*, 2966–2967.
- (12) Gao, L.; McCarthy, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 9052–9053.
- (13) Gao, L.; McCarthy, T. J. *Langmuir* **2006**, *22*, 6234–6237.
- (14) Extrand, C. W. *Langmuir* **2003**, *19*, 3793–3796.
- (15) Gupta, P.; Ulman, A.; Fanfan, S.; Korniakov, A.; Loos, K. *J. Am. Chem. Soc.* **2005**, *127*, 4–5.
- (16) Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988–994.
- (17) Cassie, A. B. D.; Baxter, S. *Trans. Faraday Soc.* **1944**, *40*, 546–550.
- (18) Krossing, I.; Slattery, J. M.; Dagueuet, C.; Dyson, P. J.; Oleinikova, A.; Weingärtner, H. *J. Am. Chem. Soc.* **2006**, *128*, 13429–13424.
- (19) Wang, Y.; Voth, G. A. *J. Am. Chem. Soc.* **2005**, *127*, 12192–12193.
- (20) Winterton, N. *J. Mater. Chem.* **2006**, *16*, 4281–4293.
- (21) Santos, L. M. N. B. F.; Canongia Lopes, J. N.; Coutinho, J. A. P.; Esperanca, J. M. S. S.; Gomes, L. R.; Marrucho, I. M.; Rebelo, L. P. N. *J. Am. Chem. Soc.* **2007**, *129*, 284–285.
- (22) Millefiorini, S.; Tkaczyk, A. H.; Sedev, R.; Efthimiadis, J.; Ralston, J. *J. Am. Chem. Soc.* **2006**, *128*, 3098–3101.
- (23) Page, P. M.; McCarty, T. A.; Baker, G. A.; Baker, S. N.; Bright, F. V. *Langmuir* **2007**, *23*, 843–849.
- (24) Dubois, P.; Marchand, G.; Fouillet, Y.; Berthier, J.; Douki, T.; Hassine, F.; Gmouh, S.; Vaultier, M. *Anal. Chem.* **2006**, *78*, 4909–4917.
- (25) Pereira, A. B.; Santamarta, F.; Tojo, E.; Rodriguez, A.; Tojo, J. *J. Chem. Eng. Data* **2006**, *51*, 952–954.
- (26) Law, G.; Watson, P. R. *Langmuir* **2001**, *17*, 6138–6141.
- (27) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156–164.
- (28) Surface tension values were determined using drop shape analysis of pendant drops with a Dataphysics instrument.
- (29) Central Glass Co., Ltd., Kowa-Hitotsubashi Bldg., Kanda-Nishikicho 3-Chome, Chiyoda-Ku, Tokyo 101, Japan. see: www.cgco.co.jp/English.
- (30) Chen, W.; Fadeev, A. Y.; Hsieh, M. C.; Öner, D.; Youngblood, J.; McCarthy, T. J. *Langmuir* **1999**, *15*, 3395–3399.
- (31) Öner, D.; McCarthy, T. J. *Langmuir* **2000**, *16*, 7777–7782.
- (32) Norton, F. J. U.S. Patent 2,412,470, Dec. 10, 1946.
- (33) Fadeev, A. Y.; McCarthy, T. J. *Langmuir* **2000**, *16*, 7268–7274.
- (34) Chen, W.; McCarthy, T. J. *Macromolecules* **1998**, *31*, 3648–3655.
- (35) Aerov, A. A.; Khokhlov, A. R.; Potemkin, I. I. *J. Phys. Chem. B* **2006**, *110*, 16205–16207.

JA070169D