10.1071/CH10285_AC

Australian Journal of Chemistry, 2011, 64(1), 122–126

Accessory Publication

pH-Dependent wettability of carboxyphenyl films grafted to glassy carbon

Daniel M. Packwood, Paula A Brooksby, Andrew D. Abell, Alison J. Downard

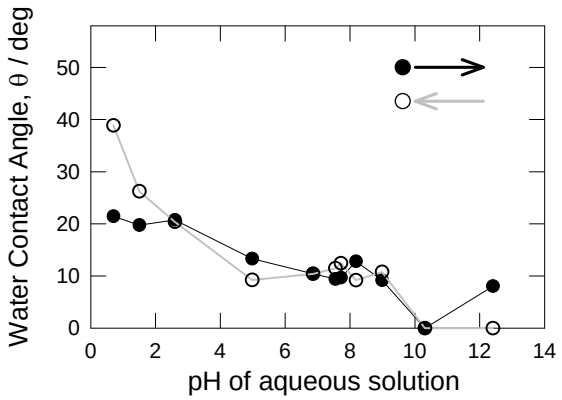

Figure 1. Plot showing the measured contact angle using water droplets at two CP films, each generated from electrolysis of 0.42 mM CBD + 0.1 M H_2SO_4 at 600 s. Each film was sonicated in pH buffered solutions sequentially from either low to high pH or the reverse. Closed and open circles indicate the direction of sampling.

Table 1. Composition of the buffered drops used for contact angle measurements.

pH	Composition	Component Concentrations /M	Buffer Concentration /M
1.45	HCl / KCl	[HCl] = 0.134M	0.184
		[KCl] = 0.05M	
1.83	HCl / KCl	[HCl] = 0.0414M	0.0914
		[KCl] = 0.05M	
3.98	AcOH / NaOAc *	[NaOAc] = 0.025M	0.2
		[AcOH] = 0.175M	
5.24	AcOH / NaOAc	[NaOAc] = 0.139M	0.2
		[AcOH] = 0.061M	
6.06	AcOH / NaOAc	[NaOAc] = 0.19M	0.2
		[AcOH] = 0.01M	
6.81	Na_2HPO_4 / KH_2PO_4	[Na_2HPO_4] = 0.049M	0.099
		[KH_2PO_4] = 0.05M	
7.63	Na_2HPO_4 / KH_2PO_4	[Na_2HPO_4] = 0.087M	0.1
		[KH_2PO_4] = 0.013M	
7.83	Na_2HPO_4 / KH_2PO_4	[Na_2HPO_4] = 0.092M	0.1005
		[KH_2PO_4] = 0.0085M	
8.33	NH_3 / NH_4Cl	[NH_3] = 0.01M	0.2
		[NH_4Cl] = 0.19M	
9.23	NH_3 / NH_4Cl	[NH_3] = 0.06M	0.2
		[NH_4Cl] = 0.14M	
9.7	Na_2CO_3 / $NaHCO_3$	[Na_2CO_3] = 0.06M	0.1
		[$NaHCO_3$] = 0.04M	
11.94	KCl / NaOH	[KCl] = 0.05M	0.062
		[NaOH] = 0.012M	
12.61	KCl / NaOH	[KCl] = 0.05M	0.182
		[NaOH] = 0.132M	

(*) OAc = acetate

Contact Angle Measurements.

Our apparatus could not measure advancing or receding contact angles, so contact angle measurements were taken from a static drop resting on a horizontal surface. To obtain a good estimate of the contact angle of the droplet via this method, as well as the precision of this estimate, we considered the following: A contact angle measurement is essentially taken from a two-dimensional 'slice' of the entire three-dimensional drop, with each slice possessing its own contact angle. The entire drop could be constructed by superimposing every possible slice that could be observed on taking the contact angle measurement. Our approach to the problem follows ideas used in statistical sampling theory. For a single drop, the entire collection of contact angles is treated as a population. When a contact angle of the drop is measured experimentally, we observe a particular contact angle ϕ_i from this population. The actual wettability of the surface can be quantified by the *population mean* of the contact angles. Since the number of slices in a drop is infinite, a direct experimental evaluation of this mean is impossible; the best we can do is acquire a random sample of *n* slice contact angles, and use its sample mean

$$\hat{\theta} = \frac{1}{n}\sum_{i=1}^{n}\phi_i \qquad \ldots(1)$$

as an estimate of the population mean. The key point is that, by measuring contact angles from various slices of a single drop, we can estimate the wettability of the surface by (1) and give the precision ε of the estimate as a $100(1-\alpha)\%$ confidence limit for $\hat{\theta}$:

$$\varepsilon = t_{\alpha/2,n-1} s \Big/ \sqrt{n}\,, \qquad \ldots(2)$$

where $t_{\alpha/2,n-1}$ is the critical value of the *t*-distribution at $(n-1)$degrees of freedom, and *s* is the standard deviation of the contact angle sample.

These ideas were implemented as follows: A 2 μL drop of the buffered solution was applied to the center of the modified area of the surface by gently touching the target with a 2 μL discharge from a syringe. The surface was then placed on a horizontal support mounted at the end of a goniometer head. The surface was turned clockwise (as viewed from above) through a random angle between 0 and 360 degrees, which was judged by sight. After each turn, a photo of the drop was acquired with a camera mounted in plane with the goniometer head; each of these photos corresponds to a 'slice' described above. From a single drop, four photos were acquired. This procedure was performed quickly (within ~40s) to avoid problems with droplet evaporation. The photos were analysed with x-ray diffraction analysis software[1] by drawing a tangent from a selected 3-phase point of the drop to a constant length up the outer-edge of the drop, and measuring the angle formed between the tangent and the baseline. Note that the formulation given by (2) does not account for the presence of two three-phase points on a single drop slice, and instead assigns a single value ϕ_i to the contact angle of the slice. As such, we alternately selected either the left-hand or right-hand three-phase point seen in a given photo to measure ϕ_i. From these four measurements, the contact angle was estimated with (1), with (2) assigned as the error ε of the estimate. ε was almost always close to 2 degrees.

[1] Smith, L.K., Campana, C.F., Moran, P.D., Jacob, M. Bruker Analytical X-Ray Systems Video for Windows NT Version 1.2.03.