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Near Surface Properties of Mixtures of Propylammonium Nitrate with n-Alkanols 2. Nanotribology and Fluid Dynamics

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Electronic Supplementary Information

Data Analysis Protocol for Thin-Film Drainage Experiments

The Taylor equation, used to fit thin-film drainage data, is given by Equation 1:[1]

$$F_H = \frac{6\pi R^2 \eta v}{h} \tag{1}$$

where F_H is the hydrodynamic (or, in a non-aqueous system such as the present one, “fluid dynamic”) force, R is the radius of the colloid probe, η is the viscosity of the fluid, v is the relative approach or retract velocity of the surfaces (not necessarily equal to the ramp velocity, see below), and h is the distance between the point of closest approach of the surfaces at each surface separation (*i.e.*, the abscissa of a force-distance profile).

Since at high velocity movement of liquid out of (approach) or into (retract) the gap between the substrate surface and the colloid probe causes the cantilever to deflect away from (approach) or toward (retract) the substrate surface, v is not necessarily equal to the ramp velocity. Instead, v is given by:

$$v = \frac{d(z+p)}{dt} = \frac{dh}{dt} \tag{2}$$

where z is the vertical distance moved by the piezo, p is the measured deflection of the cantilever, and t is the time between data points. Separation data were sometimes non-monotonic; this was thought to be an artefact of the closed-loop feature of the PicoForce scanner. In such cases a physically impossible negative value of v is returned. To obtain a more accurate fit the separation data was made monotonic by first applying a 3 point moving average to the raw separation data, and then (starting from a low separation and progressing to larger ones) deleting any data points that were less than the previous one. The relative velocity was then calculated from Equation 2 and, to avoid introducing experimental noise into the theoretical fit, a sixth-order polynomial was fit to the v *vs.* separation data. The equation of this polynomial was used instead of Equation 2 as a noise-free approximation of v.

The Taylor equation assumes a no-slip boundary condition exists at the solid-liquid interfaces. A no-slip boundary condition is one in which the velocity of the fluid in contact with a solid surface is equal to the velocity of the surface. A slip boundary condition then, is one in which the fluid next to a stationary surface has a finite velocity. In this case a slip length, b, is used to linearly extrapolate the distance behind the surface that would make the fluid stationary:

$$v_s = b \times \frac{\partial v}{\partial z} \tag{3}$$

where v_s is the velocity of the liquid next to the surface, and $\partial v/\partial z$ is the local shear rate. The effect of slip is to reduce the fluid dynamics force by increasing the rate of drainage of the thin film from between the surfaces.[2]

Vinogradova[3] introduced a correction factor, f^*, to the Taylor equation to account for the effect of slip:

$$F_H = \frac{6\pi R^2 \eta v}{h} f^* \tag{4}$$

where, for two surfaces with the same slip length,

$$f^* = \frac{h}{3b}\left[\left(1 + \frac{h}{6b}\right)\ln\left(1 + \frac{6b}{h}\right) - 1\right] \tag{5}$$

f^* approaches one as b approaches zero. The Taylor equation (Equation 1) and its modified form (Equations 4 and 5) are valid for small surface separations ($h \ll R$), and low Reynolds numbers (creeping flow; Re $<$ 1).[4] Both these conditions are satisfied in the thin-film drainage experiments conducted in this study.

A second term, F_0, has been added to Equation 4 to account for the effect of viscous drag on the cantilever:

$$F_H = \frac{6\pi R^2 \eta \nu}{h} f^* + F_0 \tag{6}$$

The magnitude of F_0 was always small compared to the first term on the right-hand side of Equation 6. Equation 6 was fitted to experimental approach force *vs.* apparent separation thin-film drainage data using a least-squares fitting procedure with the slip length and F_0 as fitting parameters.

Force-Distance Profiles: PAN-Dodecanol System

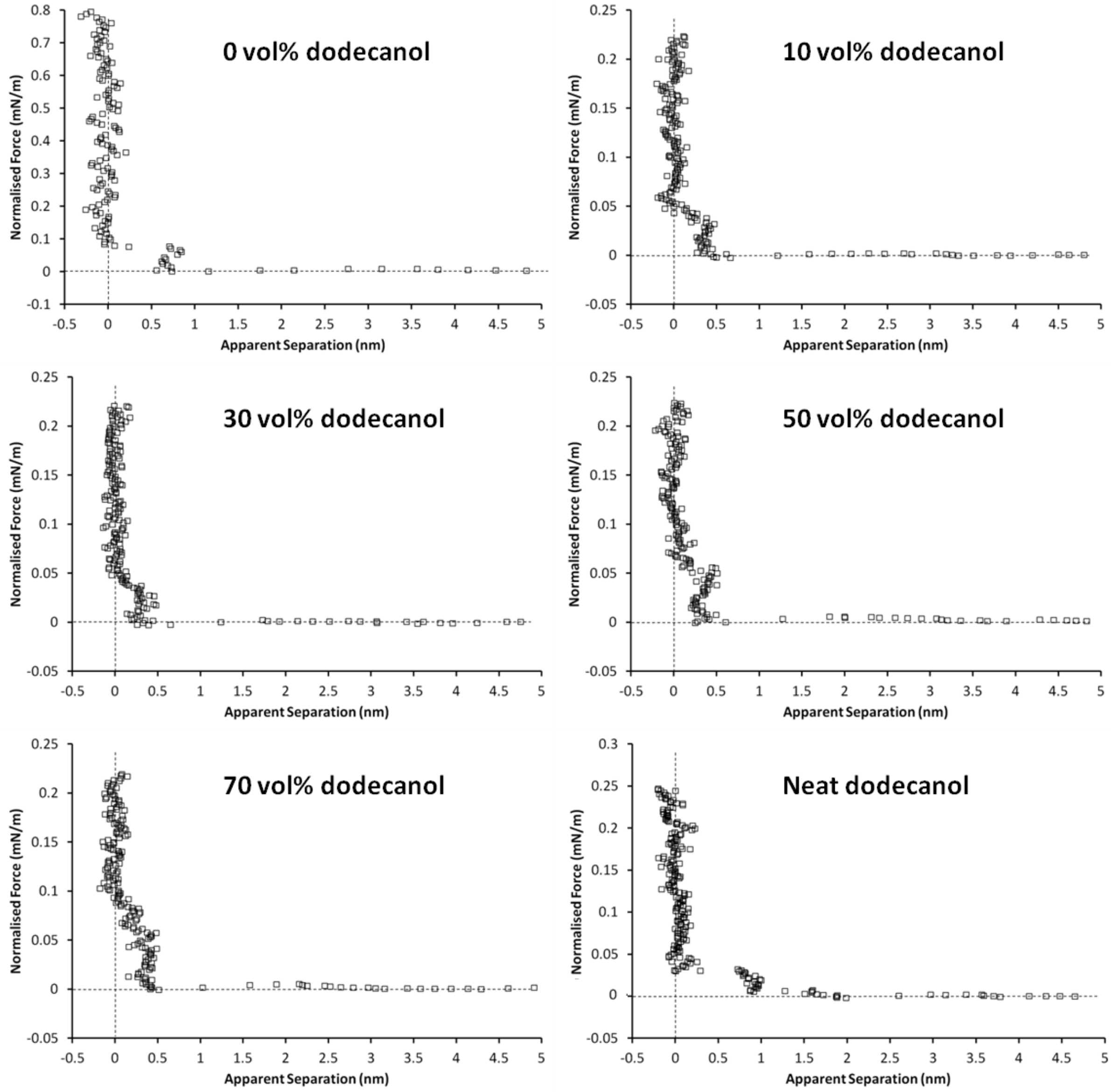

Figure A. Force-distance profiles for a silica colloid probe approaching a mica surface in PAN-dodecanol mixtures with dodecanol concentrations of 0, 10, 30, 50, and 70 vol%, and in “neat” dodecanol, which was measured against a fresh mica surface.

Viscosity as a Function of Shear Rate

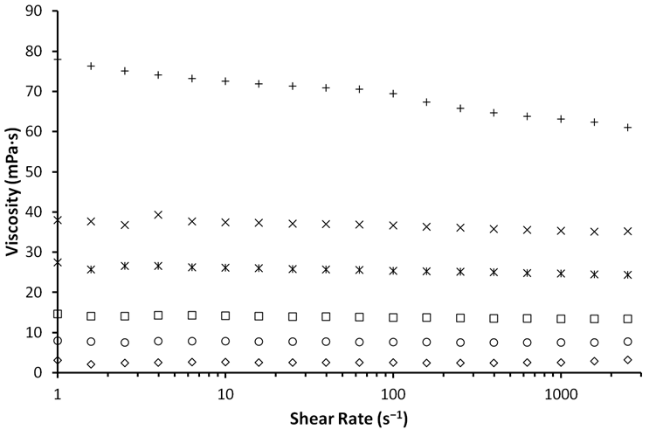

Figure B. Viscosity as a function of shear rate for PAN-butanol mixtures with different butanol concentrations at 25 °C. Pluses: 0 vol% butanol, crosses: 10 vol%, stars: 30 vol%, squares: 50 vol%, circles: 70 vol%, diamonds: 100 vol%.

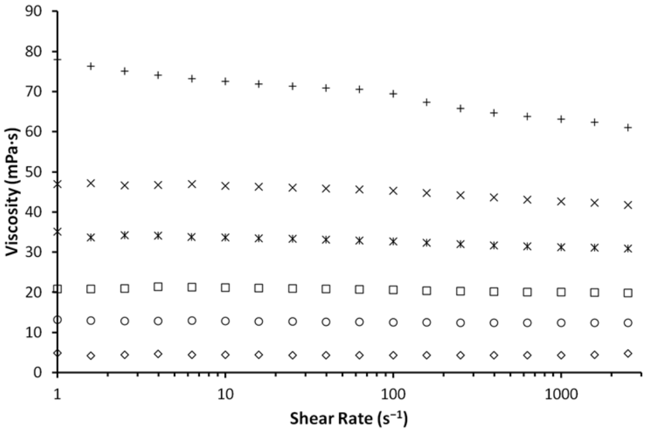

Figure C. Viscosity as a function of shear rate for PAN-hexanol mixtures with different hexanol concentrations at 25 °C. Pluses: 0 vol% hexanol, crosses: 10 vol%, stars: 30 vol%, squares: 50 vol%, circles: 70 vol%, diamonds: 100 vol%.

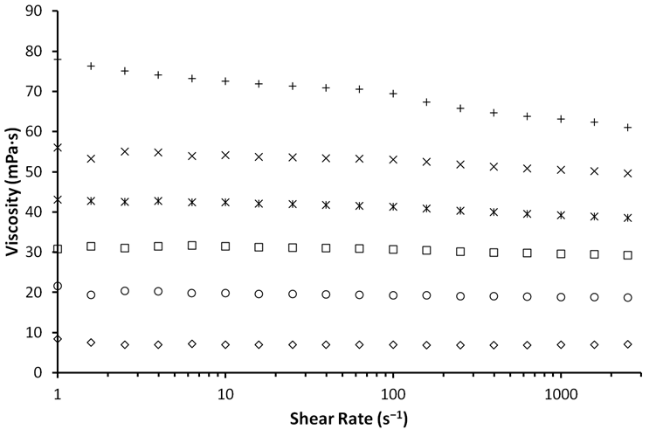

Figure D. Viscosity as a function of shear rate for PAN-octanol mixtures with different octanol concentrations at 25 °C. Pluses: 0 vol% octanol, crosses: 10 vol%, stars: 30 vol%, squares: 50 vol%, circles: 70 vol%, diamonds: 100 vol%.

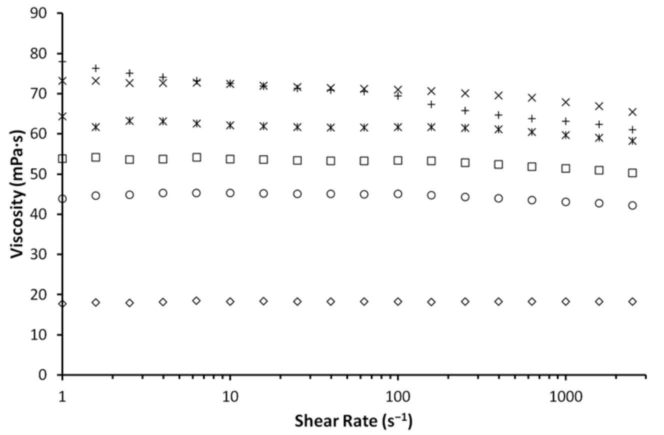

Figure E. Viscosity as a function of shear rate for PAN-dodecanol mixtures with different dodecanol concentrations at 25 °C. Pluses: 0 vol% dodecanol, crosses: 10 vol%, stars: 30 vol%, squares: 50 vol%, circles: 70 vol%, diamonds: 100 vol%.

Fits to Thin-Film Drainage Data

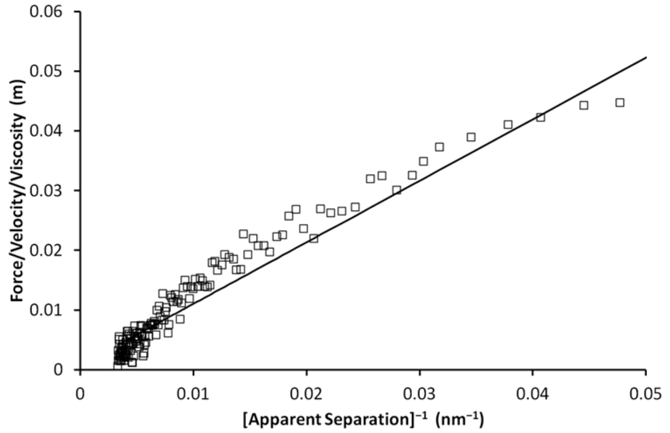

Figure F. Thin film drainage data for a 50:50 vol% mixture of PAN and butanol. The data is plotted as force/relative velocity/viscosity as a function of 1/apparent separation. Only every 7th data point is plotted. The thick, straight line represents a no-slip boundary condition. To obtain this fit, the slip length was set equal to zero, and the viscosity was used as a fitting parameter in a least-squares fitting procedure. The viscosity returned by the fit is 8.72 mPa·s; the bulk viscosity of a 50:50 vol% mixture of PAN and butanol is 14.32 mPa·s. The straight line does not provide as good a fit to the data as the curved line in Figure 5 of the main manuscript.

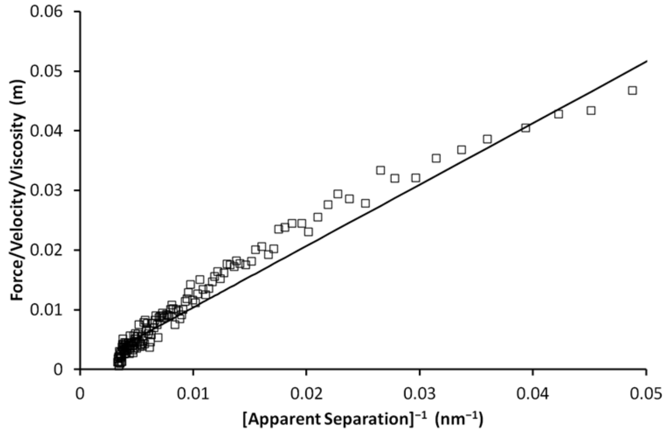

Figure G. Thin film drainage data for a 50:50 vol% mixture of PAN and hexanol. The data is plotted as force/relative velocity/viscosity as a function of 1/apparent separation. Only every 7th data point is plotted. The thick, straight line represents a no-slip boundary condition. To obtain this fit, the slip length was set equal to zero, and the viscosity was used as a fitting parameter in a least-squares fitting procedure. The viscosity returned by the fit is 13.68 mPa·s; the bulk viscosity of a 50:50 vol% mixture of PAN and hexanol is 20.97 mPa·s. The straight line does not provide as good a fit to the data as the curved line in Figure 4 of the main manuscript.

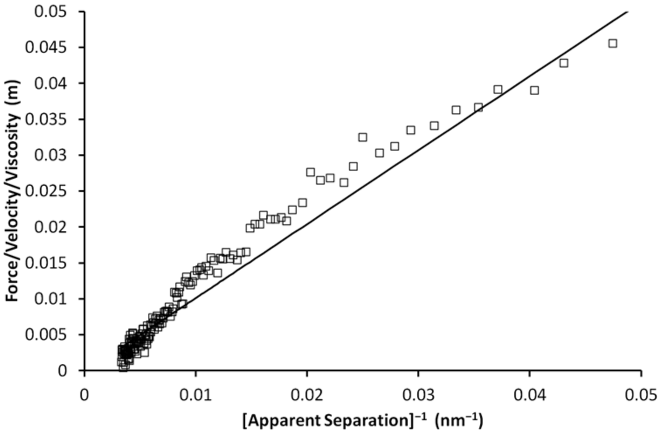

Figure H. Thin film drainage data for a 50:50 vol% mixture of PAN and octanol. The data is plotted as force/relative velocity/viscosity as a function of 1/apparent separation. Only every 7th data point is plotted. The thick, straight line represents a no-slip boundary condition. To obtain this fit, the slip length was set equal to zero, and the viscosity was used as a fitting parameter in a least-squares fitting procedure. The viscosity returned by the fit is 15.46 mPa·s; the bulk viscosity of a 50:50 vol% mixture of PAN and octanol is 31.18 mPa·s. The straight line does not provide as good a fit to the data as the curved line in Figure 5 of the main manuscript.

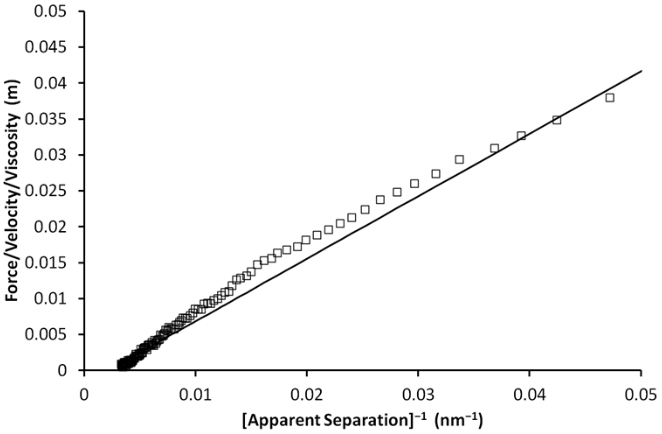

Figure I. Thin film drainage data for a 50:50 vol% mixture of PAN and dodecanol. The data is plotted as force/relative velocity/viscosity as a function of 1/apparent separation. Only every 7th data point is plotted. The thick, straight line represents a no-slip boundary condition. To obtain this fit, the slip length was set equal to zero, and the viscosity was used as a fitting parameter in a least-squares fitting procedure. The viscosity returned by the fit is 25.99 mPa·s; the bulk viscosity of a 50:50 vol% mixture of PAN and dodecanol is 53.91 mPa·s. The straight line does not provide as good a fit to the data as the curved line in Figure 5 of the main manuscript.

Fluid Dynamics Data

Table A. Bulk viscosities (obtained from viscometry measurements at ≈ 25 °C) of all solutions tested, average slip lengths for each system, and average viscous drag forces acting on the colloid probe as it moves through each liquid. Fits to six datasets were averaged to produce the values given. Results for "neat alcohol" experiments, which start from 100 vol% alcohol, are reported for octanol and dodecanol.

Alcohol	Alcohol Concentration (vol%)	Bulk Viscosity (mPa·s)	Mean Slip Length ± Standard Deviation (nm)	Mean Drag on Cantilever ($\times 10^3$ mN·m^{-1})
Butanol	0	76.5	13.0 ± 0.66	16.0
	10	38.0	15.7 ± 0.91	7.0
	30	26.7	11.5 ± 0.82	4.3
	50	14.3	9.0 ± 0.43	1.4
	70	7.8	7.4 ± 0.68	0.1
	100	2.6	6.9 ± 1.33	0.2
Hexanol	0	76.5	8.6 ± 0.76	16.0
	10	47.0	12.3 ± 0.88	9.4
	30	34.4	11.7 ± 0.62	7.2
	50	21.0	7.3 ± 0.47	3.0
	70	13.0	7.3 ± 0.54	2.6
	100	4.6	2.2 ± 0.58	0.0
Octanol	0	76.5	13.8 ± 0.65	16.2
	10	54.9	10.2 ± 0.73	10.8
	30	42.9	6.1 ± 0.32	7.1
	50	31.2	14.1 ± 0.60	6.3
	70	20.5	10.8 ± 0.45	4.2
	100	7.6	5.9 ± 0.79	0.9
	Neat octanol	7.6	9.4 ± 1.90	1.5
Dodecanol	0	76.5	16.4 ± 1.34	25.7
	10	73.2	14.5 ± 1.23	25.2
	30	63.3	14.4 ± 0.79	22.8
	50	53.9	12.8 ± 1.16	20.1
	70	44.6	10.8 ± 1.12	16.2
	100	18.0	11.9 ± 0.74	7.8
	Neat dodecanol	18.0	9.1 ± 1.35	4.9

References

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3. O. I. Vinogradova, *Langmuir*, 1995, **11**, 2213-2220
4. O. Reynolds, *Phil. Trans. R. Soc. Lond.*, 1886, **177**, 157-234