**Table II. Comparison of Predictions from the Modified Dubinin–Radushkevich (MDR), Dubinin–Radushkevich (DR), Dubinin–Astakhov (DA), and Langmuir (LAN) Adsorption Isotherms**

| | | avg rel error,[a] % | | | | Henry's law constant[b] | |
|---|---|---|---|---|---|---|---|
| adsorbate | T, K | MDR | LAN | DR | DA | MDR | LAN |
| $CH_4$[c] | 212 | 0.884 | 7.314 | 1.115 | 0.946 | 4.679 | 5.905 |
| | 260 | 1.394 | 4.858 | 1.632 | 0.547 | 0.947 | 1.422 |
| | 301 | 1.957 | 2.725 | 2.239 | 1.145 | 0.380 | 0.589 |
| $C_2H_6$[c] | 212 | 2.336 | 10.831 | 4.515 | 5.107 | 291.155 | 265.827 |
| | 260 | 1.606 | 8.746 | 1.729 | 1.556 | 31.473 | 24.649 |
| | 301 | 0.779 | 5.493 | 1.172 | 0.719 | 3.488 | 6.172 |
| $C_2H_4$[c] | 212 | 2.925 | 13.392 | 5.063 | 3.371 | 3626.522 | 116.233 |
| | 260 | 0.689 | 8.426 | 0.840 | 0.781 | 18.702 | 14.883 |
| | 301 | 0.414 | 5.456 | 0.844 | 0.472 | 2.529 | 4.260 |
| $CO_2$[c] | 212 | 1.548 | 6.506 | 3.739 | 0.977 | 67.259 | 39.580 |
| | 260 | 1.547 | 3.597 | 2.957 | 1.032 | 6.355 | 5.134 |
| | 301 | 0.757 | 3.310 | 1.789 | 0.398 | 1.803 | 1.442 |
| $CH_4$[d] | 293 | 0.804 | 1.338 | 0.782 | 0.685 | 1.059 | 0.966 |
| | 313 | 0.368 | 1.482 | 0.529 | 0.402 | 0.734 | 0.649 |
| | 333 | 0.513 | 0.747 | 0.529 | 0.524 | 0.489 | 0.453 |
| | 363 | 0.687 | 0.891 | 0.726 | 0.709 | 0.290 | 0.274 |
| $C_2H_4$[d] | 293 | 0.166 | 1.087 | 0.235 | 0.073 | 9.176 | 5.481 |
| | 313 | 0.243 | 0.810 | 0.412 | 0.365 | 6.498 | 3.398 |
| | 333 | 0.180 | 1.246 | 0.232 | 0.236 | 3.648 | 2.400 |
| | 363 | 0.733 | 1.576 | 0.760 | 0.759 | 1.373 | 1.362 |
| $C_2H_6$[d] | 293 | 0.254 | 1.126 | 0.355 | 0.354 | 17.323 | 7.109 |
| | 313 | 0.172 | 1.473 | 0.173 | 0.174 | 8.046 | 4.804 |
| | 333 | 0.078 | 1.632 | 0.096 | 0.085 | 2.101 | 2.929 |
| | 363 | 0.718 | 1.769 | 0.689 | 0.666 | 1.345 | 1.739 |
| $C_2H_8$[d] | 293 | 0.544 | 0.858 | 0.885 | 0.473 | 7.858 | 19.713 |
| | 313 | 0.314 | 0.905 | 0.559 | 0.279 | 5.709 | 13.888 |
| | 333 | 0.177 | 1.122 | 0.428 | 0.177 | 4.471 | 9.746 |
| | 363 | 0.111 | 1.340 | 0.403 | 0.167 | 3.169 | 5.314 |
| $C_3H_6$[d] | 293 | 0.473 | 0.696 | 0.664 | 0.486 | 7.132 | 21.821 |
| | 313 | 0.091 | 0.539 | 0.151 | 0.089 | 4.106 | 14.133 |
| | 363 | 0.172 | 1.449 | 0.311 | 0.163 | 3.327 | 4.633 |
| $CO_2$[d] | 293 | 0.34 | 1.068 | 0.268 | 0.102 | 3.115 | 2.758 |
| | 313 | 0.598 | 1.462 | 0.813 | 0.764 | 1.774 | 1.732 |
| | 333 | 0.899 | 1.820 | 1.278 | 1.230 | 1.179 | 1.139 |
| | 363 | 0.893 | 1.665 | 1.142 | 0.912 | 0.711 | 0.634 |

[a] Average relative error $= (100/N)\sum_{j=1}^{N}\mathrm{abs}(n_{cal} - n_{exp})_j/n_{exp}$, where $N$ = number of data points. [b] Henry's law constant, mmol/g per atm. [c] BPL activated carbon (Reich et al., 1980). [d] Nuxit activated carbon (Szepesy and Illes, 1963).

muir isotherms. Below a $P/P_s$ of $10^{-6}$, the MDR and Langmuir models again predicted very similar $\pi^*$ values, whereas the $\pi^*$ from the DR equation was significantly lower as a result of having a zero limiting slope. Some generalizations can be made from these results.

The differences in the $\pi^*$ values below a $P/P_s$ of $10^{-6}$ are insignificant because this range is far below typical experimental conditions. However, in the range of $P/P_s$ between $10^{-6}$ and $10^{-2}$, the MDR equation should be used to calculate $\pi^*$. Above a $P/P_s$ of $10^{-2}$, the DR equation can be used directly to calculate $\pi^*$ by using the analytical expression given by Talu and Myers.[3]

# Notes

## Curvature Elasticity of Charged Membranes

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The phenomenological formula for the bending energy per unit area of a membrane in quadratic approximation is[1]

$$g_{bend} = \frac{1}{2}k_c(c_1 + c_2 - c_0)^2 + \bar{k}_c c_1 c_2 \qquad (1)$$

where $c_1$ and $c_2$ are the principal curvatures, $c_0$ is the spontaneous curvature (which vanishes for symmetric membranes), $k_c$ is the bending rigidity, and $\bar{k}_c$ is the elastic modulus of Gaussian curvature.

Low-angle X-ray scattering can yield spectra for lamellar phases from which it is possible to infer these moduli.[2] A recent calculation by Helfrich[3] deals with the limit of low surface charge or high salt. However, there is extant no a priori theoretical estimates in realistic regimes. We here derive expressions for bending moduli in that situation.

(1) Helfrich, W. *Z. Naturforsch.* **1973**, *28C*, 693.
(2) Safinya, C. R.; Roux, D.; Smith, G. S.; Sinha, S. K.; Dimon, P.; Clark, N. A.; Bellocq, A. M. *Phys. Rev. Lett.* **1986**, *57*, 2718.
(3) Winterhalter, M.; Helfrich, W. *J. Phys. Chem.* **1988**, *92*, 6865.

In the Appendix we calculate the free energy per unit area of a diffuse double layer inside and outside of a cylinder or sphere with uniform surface charge density $\sigma$, assuming charge neutrality. These formulas have the form, to order $1/(\kappa R)^2$

$$g_{el}^{out} = g_0 + \frac{g_1}{\kappa R} + \frac{g_2}{(\kappa R)^2} \qquad (2)$$

$$g_{el}^{in} = g_0 - \frac{g_1}{\kappa R} + \frac{g_2}{(\kappa R)^2} \qquad (3)$$

where $\kappa$ is the inverse Debye length and $R$ the radius of the cylinder or sphere. The quantities $g_0$, $g_1$, and $g_2$ can be detemined from eq A13 and A14.

These results can be used to calculate the electrostatic free energy for cylindrical and spherical membranes. Because the dielectric constant of the membrane is much smaller than that of water, it should be a reasonable approximation to ignore any coupling between the monolayers and regard the inside and outside to be both charge neutral. We shall also assume that the surface charge density is the same on the inside and outside.

For cylindrical membranes, the free energy per unit area of membrane can be shown (cf. Appendix) to be

$$g_{el}^{cyl} = \frac{2(R_o g^{out} + R_i g^{in})}{R_o + R_i} = 2g_0 + \frac{2g_2}{(\kappa R)^2} \qquad (4)$$

and for spherical membranes the free energy per unit area of membrane can be shown to be

$$g_{el}^{sph} = \frac{2(R_o^2 g^{out} + R_i^2 g^{in})}{R_o^2 + R_i^2} = 2g_0 + \frac{2g_2 + g_1 \kappa t}{(\kappa R)^2} \qquad (5)$$

where $R_i$ and $R_o$ are the inner and outer radii, $R = (R_i + R_o)/2$, and $t = R_o - R_i$ is the membrane thickness.

Comparison with eq 1 yields

$$k_c = \frac{4g_2^{cyl}}{\kappa^2} \qquad (6)$$

$$\bar{k}_c = \frac{2(g_2^{sph} - 4g_2^{cyl})}{\kappa^2} + \frac{g_1^{sph} t}{\kappa} \qquad (7)$$

Thus we obtain for the bending rigidity

$$k_c = \frac{\epsilon}{\pi\kappa}\left(\frac{kT}{e}\right)^2\left[1 - \frac{8}{s^2} + \frac{8}{s^2(1 + s^2/4)^{1/2}}\right] \qquad (8)$$

and for the modulus of Gaussian curvature

$$\bar{k}_c = -\frac{2\epsilon}{\pi\kappa}\left(\frac{kT}{e}\right)^2\left[D_1\left(\ln\left(\frac{1 + (1 + s^2/4)^{1/2}}{2}\right)\right) + \kappa t \ln\left(\frac{1 + (1 + s^2/4)^{1/2}}{2}\right)\right] \qquad (9)$$

where $s = 4\pi e\sigma/(\epsilon\kappa kT)$, $\epsilon$ is the dielectric constant of water, $e$ is the protonic charge, $k$ is Boltzmann's constant, $T$ is the absolute temperature, and $D_1$ is the Debye function (see eq A16).

## Discussion

For small $s$ (i.e., for low surface charge density or high salt concentration), the bending moduli take the approximate form

$$k_c = \frac{3\pi\sigma^2}{\epsilon\kappa^3} \qquad (10)$$

$$\bar{k}_c = -\frac{2\pi\sigma^2}{\epsilon\kappa^3}(1 + \kappa t) \qquad (11)$$

in agreement with the result of Helfrich.[3]

On the other hand, for large $s$ (i.e., large surface charge or low salt concentration) they take the form

$$k_c = \frac{\epsilon}{\pi\kappa}\left(\frac{kT}{e}\right)^2 \qquad (12)$$

$$\bar{k}_c = -\frac{2\epsilon}{\pi\kappa}\left(\frac{kT}{e}\right)^2\left[\frac{\pi^2}{6} + \kappa t \ln\left(\frac{s}{4}\right)\right] \qquad (13)$$

The stability of membranes requires $\bar{k}_c$ to be negative (a condition that is met) and $k_c + \bar{k}_c/2$ to be positive. Thus, we conclude that the electrostatic contribution to the bending energy tends to destabilize highly charged planar membranes and also weakly charged planar membranes unless their half-thickness $(t/2)$ is less than the Debye length.

The above results have been obtained assuming the validity of the Poisson–Boltzmann description of the double layer, the limitations of which are well known.[4,5] In particular, in the low-$s$ limit there is a problem in interpreting the effective surface charge (including ion binding). Fortunately, in the case of real interest, large $s$, the results are independent of this quantity and should have a wider validity. Further extensions of the theory to include, e.g., association–dissociation equilibrium of the ionic head groups and/or optimization of the head group area[6] are straightforward. For the more difficult counterions only case for which the phenomenological formula for the bending energy, eq 1, no longer holds will be dealt with in a subsequent paper.

## Appendix

In the Gouy–Chapman theory (for a 1–1 electrolyte), the electrostatic potential $\Psi$ is given by the Poisson–Boltzmann equation

$$\nabla^2\Psi = \frac{8\pi n_0 e}{\epsilon kT}\sinh\left(\frac{e\Psi}{kT}\right) \qquad (A1)$$

where $n_0$ is the bulk electrolyte concentration, $\epsilon$ is the dielectric constant of water, $e$ is the protonic charge, $k$ is Boltzmann's constant, and $T$ is the absolute temperature. By use of the dimensionless quantities $y = e\Psi/kT$ and $x = \kappa r$, this equation becomes, in cylindrical or spherical coordinates, assuming $\Psi$ is a function of $r$ only

$$\frac{d^2 y}{dx^2} + \frac{m}{x}\frac{dy}{dx} = \sinh y \qquad (A2)$$

where $\kappa$ is the inverse Debye length given by

$$\kappa^2 = \frac{8\pi n_0 e^2}{\epsilon kT} \qquad (A3)$$

and where $m = 1$ or 2 for cylindrical or spherical coordinates, respectively.

For the outside of a cylinder or sphere, assuming charge neutrality and assuming a uniform surface charge density

(4) Attard, P.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Phys.* **1988**, *88*, 4987; **1988**, *89*, 4358.

(5) Kjellander, R.; Marcelja, S. *J. Phys. (Les Ulis, Fr.)* **1988**, *49*, 1009.

(6) Evans, D. F.; Mitchell, D. J.; Ninham, B. W. *J. Phys. Chem.* **1984**, *88*, 6344.

$\sigma$ on the surface, the boundary conditions are

$$y, \frac{dy}{dx} \to 0 \text{ as } x \to \infty \tag{A4}$$

$$\frac{dy}{dx} = -s = -\frac{4\pi e\sigma}{\epsilon\kappa kT} \text{ for } x = \kappa R \tag{A5}$$

where $R$ is the radius of the cylinder or sphere.
Integrating eq A2 with respect to $y$, we obtain

$$\left(\frac{dy}{dx}\right)^2 = 4\sinh^2\left(\frac{y}{2}\right) - \int_0^y \frac{2m}{x} \frac{dy}{dx} dy \tag{A6}$$

The planar limit $m = 0$ is easily solved to yield

$$\frac{dy}{dx} = -2\sinh\left(\frac{y}{2}\right) \tag{A7}$$

$$x - \kappa R = \frac{1}{2}\ln\left(\frac{z+1}{z-1}\right)\left(\frac{z_0-1}{z_0+1}\right) \tag{A8}$$

where $z = \cosh(y/2)$, $z_0 = \cosh(y_0/2)$, $y_0 = e\Psi_0/kT$, and $\Psi_0$ is the surface potential.

We wish to solve eq A6 for large $\kappa R$. We note that except for very small $y$ (exponentially small in $\kappa R$) $x \approx \kappa R$. Therefore, to first order in $1/\kappa R$, using this approximation and eq A7, we have

$$\left(\frac{dy}{dx}\right)^2 = 4\sinh^2\left(\frac{y}{2}\right) + \frac{8m}{\kappa R}\left[\cosh\left(\frac{y}{2}\right) - 1\right] \tag{A9}$$

To obtain the next order approximation, we use eq A8 and A9, which yield

$$\left(\frac{dy}{dx}\right)^2 =$$
$$4(z^2 - 1) + \frac{8m}{\kappa R}(z - 1) + \frac{8m(m-1)}{(\kappa R)^2}\ln\left(\frac{z+1}{2}\right) \tag{A10}$$

Applying this equation at the surface ($x = \kappa R$) where $z = z_0$ and $dy/dx = -s$ yields a relation between $s$ and $z_0$ or $y_0$. It is straightforward to invert this equation to obtain (to leading orders in $1/\kappa R$)

$$z_0 = (1 + s^2/4)^{1/2} -$$
$$\frac{m}{\kappa R}\left[1 - \frac{1}{(1 + s^2/4)^{1/2}}\right] + \frac{m^2}{8(\kappa R)^2}\frac{s^2}{(1 + s_2/4)^{3/2}} -$$
$$\frac{m(m-1)}{(\kappa R)^2(1 + s^2/4)^{1/2}}\ln\left[\frac{1 + (1 + s^2/4)^{1/2}}{2}\right] \tag{A11}$$

or

$$y_0 =$$
$$2\ln\left[\frac{s}{2} + (1 + s^2/4)^{1/2}\right] - \frac{4m}{s\kappa R}\left[1 - \frac{1}{(1 + s^2/4)^{1/2}}\right] +$$
$$\frac{2m^2}{(\kappa R)^2}\left[\frac{8}{s^3} - \frac{3}{s(1 + s^2/4)^{3/2}} - \frac{8}{s^3(1 + s^2/4)^{3/2}}\right] -$$
$$\frac{4m(m-1)}{s(\kappa R)^2(1 + s^2/4)^{1/2}}\ln\left[\frac{1 + (1 + s^2/4)^{1/2}}{2}\right] \tag{A12}$$

The electrostatic free energy per unit area is

$$g_{el} = \int_0^\sigma \Psi_0 \, d\sigma = \frac{\sigma kT}{es}\int_0^s y_0 \, ds \tag{A13}$$

where

$$\frac{1}{s}\int_0^s y_0 \, ds = 2\ln\left[\frac{s}{2} + (1 + s^2/4)^{1/2}\right] - \frac{4}{s}[(1 + s^2/4)^{1/2} - 1] - \frac{4m}{s\kappa R}\ln\left[\frac{1 + (1 + s^2/4)^{1/2}}{2}\right] + \frac{m^2}{(\kappa R)^2}\left[\frac{1}{s} - \frac{8}{s^3} + \frac{8}{s^3(1 + s^2/4)^{1/2}}\right] - \frac{2m(m-1)}{s(\kappa R)^2}f[(1 + s^2/4)^{1/2}] \tag{A14}$$

where

$$f(x) = 2\int_0^x \frac{\ln[(1 + z)/2]}{z^2 - 1} dz = D_1\left[\ln\left(\frac{1+x}{2}\right)\right] \tag{A15}$$

where $D_1(x)$ is the Debye function[7]

$$D_1(x) = \int_0^x \frac{t \, dt}{e^t - 1} \tag{A16}$$

For the inside of a cylinder or sphere we can still apply eq A2. However, the boundary conditions are modified. Assuming charge neutrality, we have

$$y, \frac{dy}{dx} \text{ finite as } x \to 0 \tag{A17}$$

$$\frac{dy}{dx} = s; \quad x = \kappa R \tag{A18}$$

For large $\kappa R$, $y$ is exponentially small at $x = 0$. Therefore, we will still obtain to the required accuracy eq A6. The only difference is that $dy/dx$ and therefore $x - \kappa R$ will now have the opposite sign. Consequently, the expressions for $y_0$ and $g_{el}$ will be the same but with $R$ replaced by $-R$.

(7) Abramowitz, M.; Stegun, I. A. *Handbook of Mathematical Functions*; National Bureau of Standards, U.S. Dept. of Commerce, 1970; p 998.

## Preparation of Monolayers and Stacked Layers of 1-Octadecanethiol

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### Introduction

It has been reported that stable monolayers of long *n*-alkyl alcohols (R–OH) are formed on a water surface and can be deposited on substrates.[1,2] Although monolayers of *n*-alkanethiols (R–SH) adsorbed on gold from dilute solution have recently been reported,[3] there are few reports concerning stable monolayers of thiols on a water surface. Sobotka and Rosenberg reported that 1-octadecanethiol did not form stable monolayers on a water surface by itself but that a mixture of 1-octadecanethiol and stearic acid formed stable mixed monolayers. They furthermore suggested that the thiol was air-oxidized to the disulfide in mixed layers on a water surface.[4] Livingstone and Swingley also reported that 1-octadecanethiol did not form a stable film on an aqueous 0.01 mol L$^{-1}$ solution of alu-

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