Estimation of surface area and counterion binding characteristics in fatty amine monolayers from desorption kinetics

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Abstract The surface area per molecule of an un-ionized fatty amine is very similar to the surface area per molecule of an un-ionized fatty acid. Surface area increases with ionization in both fatty amine and fatty acid films. However, fatty amine cations have much smaller surface areas than the corresponding fatty acid anions. Thus counterion binding is stronger with fatty amine cations than with fatty acid anions.

Surface area data show that counterion binding affinities for fatty amine cations decrease in the strong field sequence $Cl^- > Br^- > I^- > SCN^-$. Furthermore, surface areas in the presence of the most strongly bound counterions, Cl^- and Br^-, increase significantly with an increase in subphase ionic strength. These data are consistent with the formation of strong ion-pair bonds and their disruption with an increase in ionic strength.

Fatty amine cations desorb as micelles with much lower relative diffusion coefficients than the corresponding fatty acid anions. Furthermore, relative diffusion coefficients for fatty amine cations are strongly dependent on the specific cation. These data show that fatty amine cations form larger micelles when they desorb in the presence of strongly bound counterions. Anions enhance the solubility of a fatty acid anion in the sequence $Cl^- < I^- < SCN^-$, which is characteristic of chaotropic anions that disrupt water structure.

Supplementary key words myristylamine · palmitylamine · oleylamine · myristic acid · palmitic acid · oleic acid · surface area · desorption coefficients · counterion binding · chaotropic anion · ionic strength · micellar size · field strength

The ionization of long-chain aliphatic (fatty) amines in monolayers has been studied by force-area (π-A) isotherm, interfacial tension, and surface potential (ΔV) techniques. Early studies by Adam (1) suggested that acidity was less important than the nature of the anion in establishing the form of the π-A isotherm for a fatty amine monolayer spread on different acid subphases. The interfacial tension data of Peters (2) indicated that subphase pH was important in establishing the properties of fatty amines. Peters (2) estimated that the surface pK_a for hexadecylamine was 7, a value about 4 pH units lower than the pK_a for a soluble primary amine. Several studies indicate that the ΔV technique has both experimental and theoretical limitations. Glazer and Dogan (3) and Betts and Pethica (4) measured ΔV as a function of pH for fatty amines. Glazer and Dogan (3) estimated a pK_a of 8.5 for octadecylamine while Betts and Pethica (4) used a numerical differentiation of ΔV data in the region of very low ionization to extrapolate a pK_a of 10.1 for nonadecylamine. These ΔV studies are difficult to reconcile since the experimental ΔV values do not agree in the critical higher pH region of the ΔV–pH curves. Furthermore, Goddard (5) has suggested that the pK_a value extrapolated by Betts and Pethica (4) would be lowered by 0.5 units if a suitable dipole correction was introduced.

In previous studies (6, 7), we used desorption kinetics to obtain information about the surface area, ionization, and counterion binding properties of unstable fatty acid monolayers. Fatty acids desorb from monolayers in two temporal phases that were first described by Ter Minassian-Saraga (8). The desorption coefficient for the initial temporal phase, K_i, is obtained from the contracting area, A, of the monolayer as a function of time, t, by the equation:

$$K_i = -\frac{d \log A}{d\sqrt{t}} \qquad \text{Eq. 1}$$

Surface area per molecule, A_0, is then obtained by extrapolating A to zero time. The steady state desorption coefficient, K_s, occurs in the second temporal phase and is obtained from the equation:

$$K_s = -\frac{d \log A}{dt} \qquad \text{Eq. 2}$$

In the present investigation, we found that the desorption of fatty amines is described by the same kinetic relationships (Eq. 1 and 2) as the desorption of fatty acids. We have used A_o, K_i and K_s data to investigate counterion binding and its effect on the desorption process.

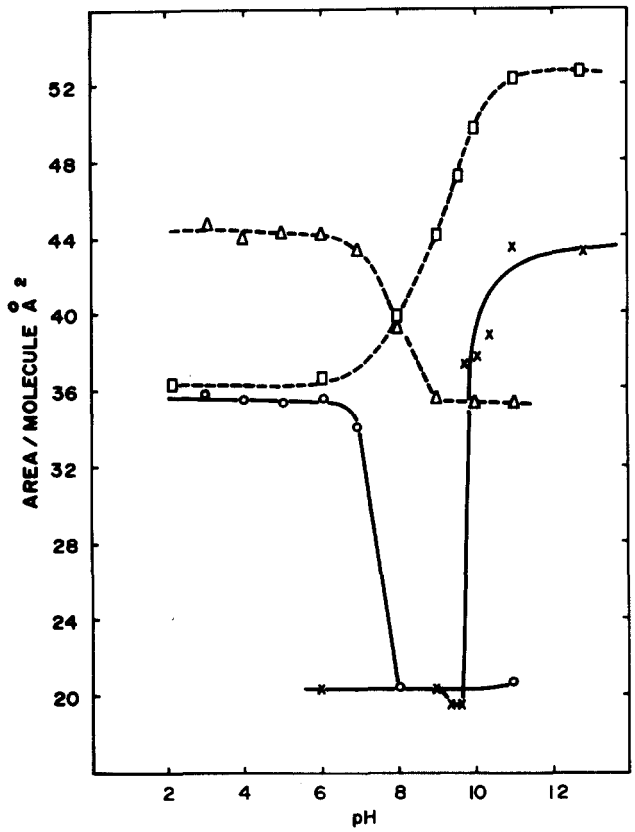

Fig. 1. Surface areas at 17 dynes/cm extrapolated from desorption data for fatty amines spread on 0.1 M NaCl containing a 0.01 M glycine buffer and fatty acids spread on 0.1 M NaCl containing a 0.01 M Tris buffer (7). ○, Palmitylamine; ×, palmitic acid; △, oleylamine; □, oleic acid. Data represent mean values from at least five desorption experiments.

MATERIALS AND METHODS

Palmitylamine (K and K Laboratories, Plainview, N. Y., and Aldrich Chemical Co., Milwaukee, Wis., technical), oleylamine (Fluka, Neu-Ulm, Germany, practical distilled), myristylamine (Fluka, purum), myristic, palmitic, stearic and oleic acids (Applied Science Laboratories, State College, Pa.) were dissolved in purified hexane (9) and these solutions were applied to a Teflon Langmuir trough as previously described (9). Constant pressure-variable area measurements were obtained with a floating barrier and piston oil as previously described (10). Castor oil and tri-*m*-tolylphosphate that generated surface pressures, π, of 17 ± 0.7 dynes/cm and 9.5 dynes/cm, respectively, were used as the piston oils. The temperature was maintained at 25°C.

RESULTS AND DISCUSSION

Initial surface area, A_o, of fatty amines as a function of pH

The surface areas of contracting fatty amine monolayers were measured as a function of time at constant surface pressure. In the initial temporal phase, log A was a linear function of $\sqrt{t}$. In the steady state phase, log A was a linear function of t. K_i (Eq. 1), K_s (Eq. 2) and A_o were calculated from these data. A_o–pH data for palmitylamine and oleylamine are plotted in **Fig. 1.** A_o for both amines approach maximum values at pH 6 and minimum values at pH 9. The maximum area represents a completely ionized film (11). Studies with fatty acid–fatty alcohol mixtures (11) suggest that the minimum area represents films that are less than 20% ionized.

Surface areas for un-ionized and completely ionized fatty amines are summarized in **Table 1.** The minimum areas for myristylamine and palmitylamine at 9.5 dynes/cm and 17 dynes/cm correspond to the surface areas of palmitylamine on an alkaline subphase that were found by Jarvis (12). Maximum

TABLE 1. Surface area, A_0, data for un-ionized and completely ionized fatty amines and fatty acids[a]

	Surface Area (Å²/molecule)			
	Un-ionized	Ionized	Un-ionized	Ionized
	9.5 dynes/cm		*17 dynes/cm*	
Myristylamine	22.3 ± 0.1 (4)[b]	45.6 ± 1.3 (11)	21.4 ± 0.1 (4)	31.6 ± 2.1 (18)
Myristic acid	32.1 ± 0.1 (4)	54.4 ± 1.0 (4)	29.1 ± 0.1 (4)	47.2 ± 1.0 (4)
Palmitylamine	21.5 ± 0.1 (4)	50.3 ± 0.3 (5)	20.6 ± 0.1 (4)	35.9 ± 0.4 (4)
Palmitic acid	22.3 ± 0.1 (4)	55.2 ± 0.5 (7)	21.1 ± 0.1 (6)	43.3 ± 0.3 (7)
Oleylamine	40.0 ± 0.2 (4)	57.3 ± 3.0 (9)	35.4 ± 0.2 (4)	44.5 ± 0.1 (4)
Oleic acid	42.2 ± 0.1 (6)	63.8 ± 0.8 (7)	36.8 ± 0.2 (8)	52.2 ± 0.9 (10)

[a] Un-ionized fatty amines were spread on 0.1 M KCl containing 0.01 M glycine adjusted with KOH to pH 10. Ionized fatty amines were spread on 0.1 M KCl containing 0.001 N HCl. Un-ionized palmitic and oleic acids were spread on 0.1 M NaCl containing 0.01 N HCl. Ionized palmitic and oleic acids were spread on 0.1 N NaOH. Un-ionized myristic acid was spread on 1.0 M NaCl containing 0.01 N HCl. Ionized myristic acid was spread on 0.1 N NaOH containing 0.9 N NaCl.

[b] Mean ± SD. Number of determinations in parentheses.

areas for completely ionized fatty amines, 46–50 Å²/molecule at 9.5 dynes/cm and 32–36 Å²/molecule at 17 dynes/cm, are significantly larger than the surface areas reported by other investigators for palmitylamine spread on acid subphases (12, 13). Differences in surface area may be explained by our use of technical grade palmitylamine, the desorption of ionized amines that occurs even with ionized stearylamine (14), and counterion binding specificities (15). The A_o value represents the true area/molecule since the surface area is extrapolated to zero time. Counterion binding specificities are discussed in the next section.

Effect of counterion binding on A_o values for the myristylamine cation

Hoffman, Boyd, and Ralston (15) previously found that at higher π values halide anions condensed ionized stearylamine monolayers in a $Cl^- > Br^- > I^-$ sequence. Halide anions condensed the ionized stearylamine monolayer in a $I^- > Br^- > Cl^-$ sequence when π was below 5 dynes/cm (15). Goddard, Kao, and Kung (16) later showed that an ionized docosylamine monolayer was condensed more by Cl^- than by Br^- in the subphase. These data are explained by anion binding in a strong field $Cl^- > Br^- > I^-$ sequence (17) to the strong cation field generated by the ionized fatty amine. The weak field $I^- > Br^- > Cl^-$ sequence noted with expanded films (low π) is explained by the decrease in the charge density of the expanded monolayer (7).

We have measured A_o as a function of counterion species and ionic strength with myristylamine, the purest commercially available fatty amine. The results are summarized in **Table 2.** Anions condense the ionized myristylamine monolayer in the strong field $Cl^- > Br^- > I^- > SCN^-$ sequence. Furthermore, the most condensed monolayers (Cl^- and Br^- subphases) expand significantly when ionic strength is increased, while the least condensed monolayer (SCN^- subphase) shows no ionic strength effect (Table 2). Counterions condense charged monolayers by neutralizing charge repulsion, with strongly bound counterions showing the greatest condensing effect (7, 11). Counterions may form discrete ion-pair bonds or exist in the double layer as mobile adsorbed ions (18). We suggest that the smaller counterions such as Cl^- and Br^- tend to form more ion-pair bonds in very strong fields (high π) than larger counterions such as SCN^-. The disruption of these discrete ion-pair bonds with increasing ionic strength then leads to film expansion. Fewer ion-pair bonds are formed with SCN^- and, as a consequence with this counterion, ionic strength has little effect on A_o. The distinction between a very strong field at high π and a somewhat weaker field at low π (less than 5 dynes/cm) is important. The weaker field is condensed by an increase in ionic strength (11), possibly through an increase in mobile adsorbed ions.

TABLE 2. Effect of anion species and ionic strength on A_o values at 17 dynes/cm for the myristylamine cation and the palmitate anion[a]

Subphase	A_o (Å²/molecule)	
	$R\text{-}NH_3^+$	$R\text{-}COO^-$
0.1 M KCl	31.6 ± 2.1 (18)[b]	46.9 ± 1.7 (16)
0.1 M KBr	34.5 ± 2.1 (19)	
0.1 M KI	42.1 ± 1.8 (14)	45.8 ± 1.0 (13)
0.1 M KSCN	45.2 ± 3.5 (14)	46.0 ± 1.2 (15)
0.3 M KCl	37.7 ± 1.7 (15)	48.2 ± 0.3 (6)
0.3 M KBr	44.4 ± 3.8 (16)	
0.3 M KI	46.3 ± 0.4 (6)	48.2 ± 0.8 (9)
0.3 M KSCN	48.7 ± 2.0 (11)	49.1 ± 1.8 (8)
0.5 M KCl		49.4 ± 0.6 (9)
0.5 M KI		48.8 ± 1.0 (9)
0.5 M KSCN		48.5 ± 0.9 (11)

[a] Myristylamine was spread on 0.001 N HCl and the specified salt. Palmitic acid was spread on 0.01 N KOH and the specified salt.
[b] Mean ± SD. Number of determinations in parentheses.

Counterion binding affinities in fatty amine cations and fatty acid anions

A_o for un-ionized amines and un-ionized fatty acids is established, with straight-chain compounds, by chain-length and unsaturation. Saturated amines with 14 or more carbon atoms form condensed films. Saturated fatty acids with 16 or more carbon atoms form condensed films with the same surface areas as the saturated amines (Fig. 1 and Table 1). Myristic acid, which contains one less methylene group than myristylamine, is partially expanded at the ambient temperature (Table 1). Oleylamine and oleic acid have very similar A_o values in un-ionized films (Fig. 1 and Table 1). Thus, the aliphatic chain establishes the surface area of the uncharged compound in both the amine and the acid series. It is apparent that the uncharged amine and carboxylic acid groups have no effect on surface area even in condensed monolayers formed from saturated aliphatic compounds.

Charged fatty amines spread on 0.1 M KCl buffered with a small amount of glycine are less expanded than the corresponding charged fatty acids spread on 0.1 M NaCl buffered with a small amount of Tris (Fig. 1). At 9.5 dynes/cm, ionized myristylamine, ionized palmitylamine and ionized oleylamine spread on KCl are more condensed than the corresponding fatty acid spread on NaCl (Table 1). It is clear even with a range in A_o values that ionized fatty amines

TABLE 3. Desorption coefficients, K_i and K_s, and the initial surface area, A_0, for completely ionized myristylamine at two surface pressures on Cl^- and SCN^- subphases

Subphase[a]	K_i	K_s	K_s/K_i	A_0
	$min^{-0.5}$	min^{-1}	$min^{-0.5}$	$Å^2/molecule$
9.5 dynes/cm				
0.3 M KCl	0.103 (4)[b] ± 0.005	0.0063 (4) ± 0.0001	0.062 ± 0.004	55.5 (4) ± 1.0
0.3 M KSCN	0.025 (5) ± 0.002	0.0031 (4) ± 0.0009	0.122 ± 0.029	57.5 (5) ± 2.0
17 dynes/cm				
0.3 M KCl	0.139 (15) ± 0.011	0.0103 (5) ± 0.0007	0.072 ± 0.008	37.7 (15) ± 1.7
0.3 M KSCN	0.043 (11) ± 0.002	0.0058 (5) ± 0.0006	0.129 ± 0.015	48.7 (11) ± 2.0

[a] The subphase contained the specified salt and 0.001 N HCl.
[b] Mean ± SD. Number of determinations in parentheses.

also have much smaller A_o values at 17 dynes/cm than the corresponding ionized fatty acids (Table 1).

In summary, A_o data show that the Cl^- counterion condenses the fatty amine cation more than the Na^+ counterion condenses the fatty acid anion (Fig. 1 and Table 1). Similar results are also obtained with Br^- and K^+ counterions (Table 2). Furthermore, condensed fatty amine cation films, Cl^- and Br^- subphases, are expanded significantly by an increase in ionic strength while ionic strength has only a small effect on the more expanded fatty amine cation, SCN^- subphase, and fatty acid anion films (Table 2). It is apparent that the Cl^- and Br^- anions are more strongly bound to cationic surfaces than Na^+ and K^+ cations are bound to anionic surfaces. These data are consistent with a strong interaction such as an ion-pair bond between the amine cation and its Cl^- or Br^- counterion.

Preferential Cl^- binding is consistent with the data of Scatchard, Scheinberg and Armstrong (19), which showed that the Cl^- was bound while the Na^+ was not bound when human serum albumin was dissolved in NaCl. Preferential Cl^- binding may explain why Bangham, Pethica and Seaman (20) found an unusually low isoelectric point of 2.8 for phosphatidylethanolamine and why other investigators (21, 22) found appreciable negative electrophoretic mobilities for phosphatidylethanolamine zwitterions. Indeed, stronger anion than cation binding to a phospholipid zwitterion surface will explain the carrier mediated anion flux that has been described in bilayers (23, 24).

Desorption coefficients, K_i and K_s, and the desorption process

Desorption studies provide information about the relative size (diffusion coefficient) and solubility of the desorbing species when desorption is a fast, quasi-equilibrium process. Gershfeld and Patlak (25) note that desorption is a quasi-equilibrium process when the activity coefficient of the monolayer, γ^*, estimated from π-A isotherms:

$$\frac{d\ \ln\gamma^*}{d\pi} = \frac{A}{RT} - C_s \qquad \text{Eq. 3}$$

where surface compressibility, C_s, is given by:

$$C_s = -\frac{1}{A}\left[\frac{\delta A}{\delta \pi}\right]_T \qquad \text{Eq. 4}$$

This is the same as γ^* estimated from K_s (Eq. 2):

$$\frac{d\ \ln\gamma^*}{d\pi} = \frac{d\ \ln K_s}{d\pi} \qquad \text{Eq. 5}$$

We have evaluated $\frac{d\ \ln\gamma^*}{d\pi}$ for myristylamine spread

TABLE 4. Effect of anion species and ionic strength on K_i values at 17 dynes/cm for the myristylamine cation and the palmitate anion[a]

Subphase	K_i ($min^{-0.5}$) R-NH_3^+	R-COO^-
0.1 M KCl	0.232 ± 0.021 (18)[b]	0.181 ± 0.010 (16)
0.1 M KBr	0.201 ± 0.01 (19)	
0.1 M KI	0.137 ± 0.007 (14)	0.183 ± 0.007 (13)
0.1 M KSCN	0.080 ± 0.006 (14)	0.195 ± 0.010 (15)
0.3 M KCl	0.139 ± 0.011 (15)	0.087 ± 0.003 (6)
0.3 M KBr	0.125 ± 0.008 (16)	
0.3 M KI	0.070 ± 0.003 (6)	0.105 ± 0.003 (9)
0.3 M KSCN	0.043 ± 0.002 (11)	0.118 ± 0.005 (8)
0.5 M KCl		0.053 ± 0.004 (9)
0.5 M KI		0.076 ± 0.004 (9)
0.5 M KSCN		0.089 ± 0.006 (11)

[a] Myristylamine was spread on 0.001 N HCl and the specified salt. Palmitic acid was spread on 0.01 N KOH and the specified salt.
[b] Mean ± SD. Number of determinations in parentheses.

on Cl^- and SCN^- subphases from the data provided in **Table 3.** Surface area (Eq. 3) and desorption (Eq. 5) data give similar values, 0.062 cm/dyne and 0.066 cm/dyne respectively for Cl^- and 0.107 cm/dyne and 0.084 cm/dyne respectively for SCN^-, suggesting that amine desorption is a quasi-equilibrium process.

Counterion binding and the relative size of the desorbing species

Desorption under quasi-equilibrium conditions is a diffusion limited process (7,8). The diffusion coefficient, D, is related to the desorption coefficients K_i and K_s by the expression:

$$\frac{K_s}{K_i} = \frac{\sqrt{\pi D}}{2\epsilon} \qquad \text{Eq. 6}$$

where ϵ is the width of the quiescent subphase adjacent to the monolayer (7, 8).

The K_s/K_i ratios (Table 3) indicate that the counterion has a profound effect on the desorbing species. The substitution of SCN^- for Cl^- results in a four-fold increase in the relative diffusion constant. Since D is inversely proportional to the square root of the molecular weight (7), the K_s/K_i ratios indicate that the molecular weight of the desorbing species may vary as much as sixteen-fold in Cl^- and SCN^- subphases. In an early light scattering study with fatty amines, Debye (26) stated that the counterion had very little effect on either critical concentration or molecular weight. Desorption studies suggest that strongly bound counterions result in larger micelles probably by neutralizing charge repulsion through ion-pair bonds.

Chaotropic anions and the solubilities of anion and cation soaps

With fatty acid films, the K_s/K_i ratio is independent of the degree of ionization (6). Desorption and, as a consequence, K_i varies directly with A_o (6, 7). Higher K_i values indicate both increased ionization and increased solubility. These effects can be demonstrated with palmitate soaps. At 17 dynes/cm, the palmitate anion spread on a 0.1 N NaOH subphase has lower A_o and K_i values, 43.3 Å²/molecule and 0.149 $min^{-0.5}$, than the palmitate anion spread on a 0.1 N KOH subphase, 47.4 Å²/molecule and 0.212 $min^{-0.5}$. Indeed, Na^+ soaps are less soluble than K^+ soaps (27).

Chaotropic anions enhance the solubilities of nonelectrolytes such as benzene (28) and acetyltetraglycine ethyl ester (29) in a $Cl^- < Br^- < SCN^- < I^-$ sequence. K_i values for the palmitate anion increase in the sequence $Cl^- < I^- < SCN^-$ (**Table 4**). These data show that chaotropic anions enhance the solubility of the palmitate anion in the sequence, $Cl^- < I^- < SCN^-$, predicted from the structure-breaking action of chaotropic anions on water (29, 30).

With fatty amine films, the chaotropic anion interacts with the fatty amine cation and, as a consequence, the K_s/K_i ratio is strongly dependent on counterion binding affinity (Table 3) and K_i varies inversely with A_o (Table 3). K_i values for the myristylamine cation decrease in the sequence $Cl^- > Br^- > I^- > SCN^-$ (Table 4). We suggest that the higher K_i values reflect the desorption of larger myristylamine cation micelles that are stabilized by strongly bound counterions. K_i may not vary directly with solubility or ionization when counterion binding has a strong influence on the desorption process.

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