a multicomponent problem and predict the elution profiles of the various components of a mixture. Results in this area will be presented shortly.6

These results will be important and useful for the study of the optimization of the experimental conditions for the separation of large molecules. In this case, mass transfer resistances play an important role that cannot be ignored.

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Thermal Decomposition of Sodium trans-Hyponitrite

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Samples of amorphous sodium *trans*-hyponitrite $(Na_2N_2O_2)$, heated with a continuous rise in temperature in the absence of oxygen, decompose suddenly between 360 and 390 $^{\circ}$ C. The decomposition products are Na₂O and N₂O, along with secondary reaction products derived from N_2O . When $Na_2N_2O_2$ is heated in an O_2 -containing atmosphere, the decomposition temperatures are lowered due to the slow oxidation of $N_2O_2^{-2}$ to NO_2^{-} and of NO_2^{-} to NO_3^{-} , which accumulate and increase the decomposition rate. At $P(O_2) = 754$ Torr, the isothermal induction period for $Na_2N_2O_2$ between 275 and 315 °C is given approximately by log $(t(\min)) = -14.8 \pm 0.3 + (41090 \pm 600 \text{ cal})/2.3RT$. At 298 ± 2 °C, the induction period of Na₂N₂O₂ depends inversely on oxygen pressure (100-745 Torr), with a purified sample showing $t(\min) = 4.83 + 4902/P^{\circ}(O_2, \text{Torr})$.

Introduction

Sodium *trans*-hyponitrite is the salt that is prepared by most synthetic routes that lead to the hyponitrite ion.¹ This derivative is rather useful because it is much more stable than the silver salt or the organic esters to storage. Chemical and safety handbooks cite a decomposition temperature of 300 °C for trans-Na₂N₂O₂,^{2,3} which appeared to be lower than values we obtained from our samples by preliminary studies with differential scanning calorimetry (DSC) methods.

In this paper we report a detailed study of the decomposition of $Na_2N_2O_2$ as a function of temperature and atmosphere. Of particular interest is the discovery of the facile cleavage of the N=N bond in $Na_2N_2O_2$ by molecular oxygen to give sodium nitrite.

Experimental Section

Sodium trans-hyponitrite was prepared by the electrolysis of 3.6 M aqueous sodium nitrite over a pool of Hg in a modification of Polydoropoulos' procedure.⁴ The product was isolated by dilution with absolute ethanol and cooling to 0 °C. The colorless crystals were washed thoroughly with ethanol and dehydrated at oil pump pressures at 25-50 °C for several days. Accurately weighed samples of 0.10 ± 0.02 g were analyzed for sodium by acidifying solutions in distilled water with concentrated HCl and concentrating to a dry residue that was weighed. Hyponitrite ion was analyzed for by precipitation of the silver salt, which was washed with water, dried at <1 Torr, and weighed.

Calorimetric measurements were obtained with a Du Pont Model 910 DSC connected to a Model 990 programmer/recorder. The sample was weighed to ± 0.01 mg and placed in a crimped Pt pan in the apparatus under a flow of nitrogen. All runs were started at 60 °C with dT/dt = 20 °C m⁻¹.

Decompositions in glass capillary tubes were carried out with a Mel-Temp apparatus with a 400 °C thermometer (Will Cat. No. Z-6858).

Isothermal decompositions were carried out with 7.2-mm-o.d. Pyrex tubes sealed at one end and with a 19/35 ground-glass joint at the other. A sample of $Na_2N_2O_2$ (34 ± 4 mg) was weighed to ± 1 mg and placed in the tube, which then was attached to a vacuum line and evacuated for 6 min at <0.01 Torr. A type T thermocouple was wrapped around the base of the tube during this time. A resistively heated, circular furnace was then raised

so that it surrounded the tube. The furnace was insulated with a large amount of glass wool, and the temperature was maintained at ± 2 °C with a Therm-o-watch (I²R, Inc.) controller. The evacuation was continued for at least 10 min to eliminate water of hydration. (Induction times did not change with longer pumping times. Elimination of the pumping during heating shortened the induction times.) Reagent-grade gases were then admitted to the tubes through glass three-way stopcocks. The pressure in the closed system ($V = 38 \text{ cm}^3$) was monitored with a transducer (MKS Instruments Type 227, range 0-1000 Torr). The end of the induction period was defined as a change of ≥ 4 Torr during a 30-s period, although this criterion probably resulted in somewhat overestimated values. For some of the longer runs, the pressure was recorded through an interface to an Apple II+ computer.

Decomposition Products. A sample of Na₂N₂O₂ (0.1022 g) was placed in a 28-mL nickel crucible, and the crucible was covered with a watch glass. The crucible was then heated carefully with a small gas flame until a sudden exothermic reaction occurred with some gas evolution and fusion. A few particles of solid were observed heated to incandescence during the decomposition. The yellowish mass obtained was allowed to cool, weighed immediately (0.0912 g), dissolved in 10 mL of deionized water, and titrated to pH 7 (0.100 N HCl, Spectrum Co. universal indicator). The titration required 11.4 mL of the acid. Ignoring the minor contribution to alkalinity from hydrolysis of NO_2^- , we infer that 0.0353 g of Na₂O was present in the product. If the remainder of the solid consisted of x g of $NaNO_2$ and y g of $NaNO_3$, then by material and sodium balance we have, respectively

$$x + y = 0.0912 - 0.0353$$

 $(22.997/69.01)x + (22.997/85.01)y + (2.22 \times 997/61.98)$ $\times 0.0353 = (2 \times 22.997/106.01) \times 94\% \times 0.1022$

The solution of these equations is x = 0.0060 g and y = 0.0499g. From oxygen balance we calculate that 0.0075 g of oxygen was present in the decomposed solid that was not initially part of the hyponitrite ion or associated water.

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⁽¹⁾ Yost, D. M.; Russell, H., Jr. Systematic Inorganic Chemistry; Prentice-Hall: New York, 1944; pp 52ff.

⁽²⁾ Handbook of Chemistry and Physics, 66th ed.; CRC Press: Cleveland, OH. 1985. (3) Lange's Handbook of Chemistry, 12th ed.; McGraw-Hill: New York,

^{1979.}

⁽⁴⁾ Polydoropoulos, C. M. Chem. Ind. (London) 1963, 1686.



Figure 1. DSC of sodium *trans*-hyponitrite (1.2 mg, sample 3G). The lower curve was obtained on reheating the decomposed sample.

TABLE I: Decomposition Temperatures for Sodium Hyponitrite by DSC Techniques

			$Na_2N_2O_2$, analyzed as		
sample	wt, mg	<i>T</i> _d , ℃	Ag ₂ N ₂ O ₂	NaCl	
3A	0.90	386	87	89	
	0.83	382			
	1.07	383			
3B	1.87	362.5	90	90	
	1.85	360			
3D	0.88	381			
3E	1.12	390		94	
	1.22	380			
3F	2.49	378	69	69	
3G	1.20	387	86	89.5	
3H	0.94	382		83	

Although we could detect NO_2^- and NO_3^- among the decomposition products by ion chromatography (Dionex 10 with conductivity detection, CO_3^{2-} -HCO₃⁻ eluant), small amounts of NaNO₂ in Na₂N₂O₂ were more easily analyzed by a colorimetric procedure in which NO_2^- is converted to an azo dye.⁵ The preliminary reduction step with Cd metal was omitted.

Raman spectra were obtained from samples in glass capillary tubes with a Coherent Model CR-4 argon ion laser.

Results

Nonisothermal Decompositions. A representative DSC curve from sodium hyponitrite is shown in Figure 1. There is a small endotherm around 100 °C corresponding to loss of some residual water of hydration and an abrupt exotherm around 387 °C. Other samples showed similar behavior, with the temperature of the onset of the exotherm varying between 360 and 390 °C and between 380 and 390 °C in all but three samples (Table I). Values of the heat released on decomposition were not very reproducible and are not reported.

The decomposition of the sodium hyponitrite was also examined with samples in glass capillaries in a conventional apparatus for determining melting points. Three determinations with ca. 2 mg of lot 3G, which appeared to be among the purest of our samples, gave (uncorrected) decomposition temperatures of 354-356, 354-356, and 333-337 °C. A sample of the same lot that was sealed at <1 Torr in a capillary tube decomposed at 384-386 °C,



Figure 2. Arrhenius plots of induction times for sodium hyponitrite (lot 3E) (O, bottom line) in 754 Torr of oxygen (\Box , middle line) twice-recrystallized sample, same atmosphere, and (\Box , top line) in 110 Torr of nitrous oxide.

in agreement with the results by DSC techniques.

A sample of lot 3G was placed in the bottom of a sealed-off 9 in. disposable pipet and heated in the melting-point apparatus while continuously pumping with an oil pump. This sample decomposed at $382 \, ^{\circ}$ C.

In each of these cases the decomposition in capillary tubes was observed by the sudden formation of a viscous froth, which climbed the tube due to rapid gas evolution. When the decomposition was complete, the residue was a white solid.

In a separate experiment, a small sample of $Na_2N_2O_2$ was decomposed in a tube that was connected to an IR gas cell. The spectrum of the evolved gases showed strong bands ascribed to nitrous oxide. The brown color of NO_2 was absent from the cell.

The samples of $Na_2N_2O_2$ and its decomposition products remained colorless when they were contained in open glass tubes. The samples in sealed capillaries showed a transient yellow color in portions of the solids present after decomposition. The yellow color disappeared within about 20 s after it was first observed.

The sample that was decomposed under dynamic vacuum and a larger sample of $Na_2N_2O_2$ that was placed in a Ni boat and decomposed in a stream of N_2 both remained bright yellow after decomposition. On exposure to air the yellow color disappeared. The color and air sensitivity are characteristic of the inorganic radical sodium hydronitrite, Na_2NO_2 .⁶ We were unable, however, to see an electron spin resonance (ESR) signal from a sample of $Na_2N_2O_2$ that had been decomposed under dynamic vacuum and sealed off without exposure to air, even though the yellow color was visible in the solid. We later discovered a aper by Jansen, who carried out a crystal structure determination on a goldenyellow, air-sensitive complex with the formula $Na_2O\cdot NaNO_2$.⁷ The complex was synthesized from the two components at 310 °C, so that the properties and mode of formation nicely account for our observations.

Isothermal Decompositions. Thermolysis of $Na_2N_2O_2$ at constant temperatures in a closed system occurred after induction periods that, at first, were highly irreproducable. The source of the variation was traced to small amounts of decomposed $Na_2N_2O_2$ that blew into the upper portion of the vacuum system and subsequently contaminated fresh samples. The problem was then eliminated by washing the vacuum lines with distilled water after each run.

In an oxygen atmosphere, samples of $Na_2N_2O_2$ at 344 °C after the induction period showed a rapid *increase* in the pressure of the closed system, while at temperatures of 320 °C and lower,

⁽⁵⁾ Standard Methods for the Examination of Water and Wastewater, 16th ed.; Franson, M. A. H., Ed.; American Public Health Association: Washington, D. C., 1985; p 391.

⁽⁶⁾ Chardon, J. C.; Theobald, J. G. Compt. Rend. Ser. C. 1966, 263, 461.
(7) Jansen, M. Ang. Chem., Int. Ed. Engl. 1976, 15, 376.



Figure 3. Dependence of induction time for $Na_2N_2O_2$ on oxygen pressure at 300 ± 2 °C. Upper curve, recrystallized sample. Lower curve, sample containing initially 0.12% sodium nitrite (lot 3E).

the end of the induction period was characterized by a slow *decrease* in total pressure. The logarithms of the induction periods were all related to temperature in the same way as the induction times for decomposition of organic explosives,⁸ with an apparent activation energy relating the decreasing induction times to increasing temperatures (Figure 2).

At 300 °C the induction times for decomposition of a limited number of samples of $Na_2N_2O_2$ were inversely proportional to the initial oxygen pressure (Figure 3). The curves for two samples of different purity were similar in shape.

Slow Formation of NaNO₂. The observations described above led us to propose that $Na_2N_2O_2$ was oxidized by oxygen to a product that causes the entire mass to decompose rapidly at the end of the induction period. Indeed, when samples of $Na_2N_2O_2$ at 259 °C were heated in O_2 for various times, followed by evacuation, cooling, and analysis of the solid for $NaNO_2$, a progressive increase in nitrite content was found (Figure 4). The rate of nitrite formation showed a posible upward inflection corresponding to the induction period determined by the rate of drop in total pressure. The amount of sodium nitrite that is formed in the sample at 70 min corresponded to a change in oxygen pressure of <2 Torr, which was much less than the change in pressure that was observed experimentally.

The critical mass of NaNO₂ in the sample corresponding to Figure 4 was about 1.3%. When a sample of Na₂N₂O₂ was ground together with 1.6% NaNO₂, its induction period under the same conditions was reduced from 83 to 40 min.

We tested the possible role of diffusion of oxidation products from the surface of the solid to the interior in the following way. Samples of $Na_2N_2O_2$ were allowed to react with oxygen (748 Torr, 275 °C) in the usual way for 24 min, and then the oxygen was pumped off. After 3–5 h oxygen was readmitted at the same pressure as before, and the time to decomposition was noted. The induction times for the interrupted experiments varied from 36 to 57 min (average, 46 min) compared with a normal induction period of 48 min.

Our analytical procedure revealed a small amount of sodium nitrite in the starting N_2O_2 , and we were obliged to repeat

TABLE II: Induction Times for $Na_2N_2O_2$ as a Function of $P^{\circ}(N_2O)$ at $340 \pm 2 \ ^{\circ}C$

$P(N_2O)$, Torr	t _{ind} , min	$P(N_2O)$, Torr	t _{ind} , min
0	51	131	16.5
20	15.5	151	14
28	15.5	181	12
40	18	254	16.5
80	16.5	320	18.5
114	15.5	458	20

the experiments at different temperatures with a twice-crystallized sample of $Na_2N_2O_2$ whose $NaNO_2$ content was 0.0104%. From the new data (Figure 2, middle curve), we calculated a similar $E_{apparent} = 41\,090$ cal/mol, although the induction times were about twice as long as before. The decomposition points of two samples of the recrystallized material in capillary tubes under dynamic vacuum were 350 and 362 °C.

The decomposition of $Na_2N_2O_2$ in the presence of nitrous oxide was also studied, and a similar relation between induction time and temperature was observed (Figure 2, top curve). For safety reasons we kept the total pressure of N_2O below atmospheric. In subsequent experiments, however, we found that the induction time was independent of the initial pressure of nitrous oxide over a 23-fold range of pressures (Table II). When N_2O alone was introduced into the apparatus at temperatures between 336 and 350 °C in separate experiments, a slow rise in pressure was observed that appeared to be zero order.

Raman Spectra. The decomposition products in glass capillary tubes were conveniently examined by Raman spectroscopy. Spectra of $Na_2N_2O_2$ before and after decomposition are shown in Figure 5.

The spectrum of the material originally showed peaks at 1376, 1138, 694, 324, and 238 cm⁻¹. Goldbloom et al.⁹ reported Raman-active bands in the anhydrous salt at 1671, 1560, 1380, 1144, 697, and 315 cm⁻¹. The agreement is fairly good with differences of 3-9 cm⁻¹. The three bands without counterparts in the other spectrum at 1671, 1650, and 238 cm⁻¹ are all weak or very weak.

The principal bands in the samples after decomposition were ascribed to sodium nitrite and sodium nitrate. Decomposition in air led to a much larger proportion of nitrate than the sample heated in an evacuated and sealed capillary. The presence of these anions was confirmed by comparison with the spectra of authentic samples of the two salts. One peak at 827 cm⁻¹ in the spectrum of NaNO₂ was shifted significantly to 814 cm⁻¹ in the mixture.

Discussion

The original purpose of the study was to obtain an accurate assessment of the stability and safety of nearly anhydrous sodium hyponitrite. We had expected a simple reaction, such as (1) or (2).

$$Na_2N_2O_2 \rightarrow Na_2O + N_2O \tag{1}$$

$$trans-Na_2N_2O_2 \rightarrow cis-Na_2N_2O_2 \tag{2}$$

The fact that there was almost no weight loss on decomposition of $Na_2N_2O_2$ (in air) in early experiments did not support reaction (1) and led us to infer (2).

The Raman spectrum rules out (2) by the absence of major spectral bands that are characteristic of the cis isomer.¹⁰ The absence of reversible processes is demonstrated by the second curve in the DSC plot (Figure 1).

The reactions that actually occur on thermal decomposition of *trans*-sodium hyponitrite can be represented by (1) together with (3) and (4). Above 320 °C reaction 1 predominates even in

$$Na_2N_2O_2 + O_2 \rightarrow 2NaNO_2 \tag{3}$$

$$2NaNO_2 + O_2 \rightarrow 2NaNO_3 \tag{4}$$

⁽⁸⁾ Castorina, T. C.; Haberman, J.; Avrami, L.; Dalrymple, E. W. In *Proceedings of the 6th International Symposium on the Reactivity of Solids*; Mitchell, J. W., et al., Eds.; Wiley-Interscience: New York, 1986; p 299.

⁽⁹⁾ Goldbloom, L.; Hughes, M. N.; Stace, B. C. Spectrochim. Acta 1976, 32A, 1345.

⁽¹⁰⁾ Kuhn, L.; Lippincott, E. R. J. Am. Chem. Soc. 1956, 78, 1820



Figure 4. Increase in sodium nitrite in 33.5 ± 0.2 mg samples of sodium hyponitrite at 259 °C in 754 ± 8 Torr of oxygen. Note that each pair of points at a given time represents a separate experiment. The error bar serves individual points for both measurements.



Figure 5. Laser-Raman spectra of sodium *trans*-hyponitrite before and after thermal decomposition. Peaks from (a) sodium nitrite and (b) sodium nitrate are indicated.

oxygen, as indicated by gas evolution and formation of solid products including yellow $Na_2O\cdot NaNO_2$. Decomposition of N_2O to give oxygen can account for formation of some $NaNO_2$ via reaction 3 when $Na_2N_2O_2$ is heated in the (initial) absence of

oxygen, although a small amount of direct attack by nitrous oxide on $Na_2N_2O_2$ is not excluded. We suspect that the lowered decomposition temperatures in the presence of N_2O (Figure 2, top curve) are due to decomposition of the gas by some adventitious, catalytic process to give oxygen, which then in turn decomposes the $Na_2N_2O_2$.

The equilibrium constant for the reaction $2NaNO_2(l) + O_2(g) \rightarrow 2NaNO_3(l)$ increases with decreasing temperature, and from published¹¹ data we calculate $K_{eq} = 4.3 \times 10^4$ at 259 °C and $P(O_2) = 1$ atm. The further oxidation of sodium nitrite to nitrate in our samples is thus explained easily on thermodynamic grounds.

Reaction 4 is consistent with (a) the predominance of $NaNO_3$ on decomposition of sodium hyponitrite in air (Figure 5), (b) the failure of the drop in oxygen pressure to correspond to the yield of sodium nitrite shown in Figure 4, and (c) the reduction of the induction period by only 50% when 1.6% sodium nitrite was added to sodium hyponitrite under the conditions described in the Figure 4. If sodium nitrite were the only impurity present, the induction time of the latter sample should have been reduced to zero.

Below 320 °C in the presence of oxygen, reactions 3 and 4 predominate. The corresponding reaction products, as expected, were colorless and sometimes remained liquid at the elevated temperatures. The high-temperature region of the phase diagram for NaNO₂-NaNO₃ has the normal shape, with a eutectic composition of about 32% NaNO₂ melting at 226 °C.¹²

The inverse dependence of the induction time for sodium hyponitrite on the pressure of oxygen (Figure 3) is understandable if the rate of reaction 3, and hence the rate of introduction of a second component into the solid,¹³ is proportional to the oxygen pressure. The power functions shown in Figure 3 were derived empirically from log-log plots. It is easy to show that if reaction 3 is first order in oxygen and nth (including zero) order in sodium hyponitrite, the time t_c to accumulate a given quantity of sodium nitrite [NaNO₂]_c at constant oxygen pressure is given by an expression of the form $t_c P(O_2) = f(k_3, [NaNO_2]_0, [NaNO_2]_c)$. The upper points in Figure 3 could indeed be described satisfactorily (r = 0.998) by the simple inverse function $t_c(\min) = 4.83 +$ $4902/P^{\circ}(O_2, \text{Torr})$. The constant term in this expression may reflect a systematic error in determining the induction times, although the data points were limited and the system is complicated by the concurrent reaction 4.

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Conclusions

The temperature of decomposition of sodium *trans*-hyponitrite under DSC conditions appears to be between 360 and 390 °C but is strongly affected by the presence of oxygen, water, and impurities.

In an atmosphere containing oxygen, $Na_2N_2O_2$ reacts below the inherent decomposition temperature to give $NaNO_2$ and $NaNO_3$. The latter products catalyze the decomposition reactions by providing a liquid phase.

The stability of $Na_2N_2O_2$ in dry air at room temperature is inferred by extrapolation of the plots in Figure 2, from which we

estimate an induction time of over 10^9 years. At ambient temperatures the compound may be classed as a reducing agent.

Acknowledgment. The assistance of Philip Karjala and Dr. Bahne Cornilsen in obtaining the Raman spectra is gratefully acknowledged. An anonymous referee brought ref 13 to our attention and made several other useful suggestions. We thank the Research Office and the Dean of Engineering of Michigan Technological University for partial support of this work.

Registry No. Na₂N₂O₂, 13517-28-7; O₂, 7782-44-7; N₂O, 10024-97-2.

COMMENTS

Reply to Comments on "On the Structure of Aggregates of Adsorbed Surfactants: The Surface Charge Density at the Hemimicelle/Admicelle Transition"

Sir: In our paper¹ we did not intend to suggest either that admicelles would be favored over hemicelles away from the point of zero charge or that hemimicelles would be favored over admicelles near the point of zero charge. What our paper showed was that for an admicelle to form at a lower surfactant concentration than that at which a hemimicelle would form, the charge of the surfactant headgroups in the admicelle must be virtually canceled by a combination of the countercharge on the surface and the charge from counterions inside the diffuse layer. We inferred from this that as the countercharge on the surface increased, the charge on the first layer of the aggregate had a greater possibility of being almost completely canceled by the charge on the surface and conditions would, in this manner only, become "more favorable" to admicelles. The most significant conclusion of our model was that the hydrophobic contribution to the decrease in the free energy of the system on formation of the second layer is not large enough to assure that admicelles will be lower energy structures than hemimicelles, because of the generally less favorable Coulombic interactions in the admicelle.

We did intend in our paper to modify our earlier view of the structure of adsorbed surfactant aggregates, so as to allow for hemimicelles in our current view. We do not agree, however, that the "hemimicellar reverse orientation model" explains more adequately than admicelles the spectroscopic studies which have appeared to date, irrespective of the questions about the correct interpretation of the spectroscopic data which arise because of our limited knowledge concerning specific interactions of the probes with host aggregates, our uncertainty about the location of the probes in the aggregates, and our uncertainty about how well the reference solvents mimic host conditions.

Admicelles actually offer a better explanation of some of the spectroscopic data than any form of hemimicelles. For example, Waterman et al.² report that the apparent polarity of the probe's environment, though more polar than in dodecane, is less polar than in a micelle. Since the probe's hydrocarbon tail is longer than the tail of the surfactants, one might expect from the hemimicelle model that, at low surfactant adsorption, the polarity experienced by the probe would be *more* water-like than in a micelle, becoming more hydrocarbon-like as coverage increased.

This is especially true in that "the strong hydrogen-bonding interactions of the nitroxide groups confer upon them a pronounced tendency to seek the [micelle/water] interface."3 Instead. Waterman et al. report that the probe sees a constant, relatively nonpolar environment over the entire isotherm. In the conclusion of their paper the authors state "since the polarity measurements indicate that the nitroxide moieties are not in an aqueous environment, this suggests either that the alkyl chain of [the probe molecule] curves such that the nitroxide sits in a region [of the hemimicelle] partly shielded from the aqueous environment ... or the SDS forms bilayers at the alumina surface such that the nitroxide is present in a hydrophobic region These data suggest that the aggregate structure does not change significantly throughout the adsorption isotherm." These results are better explained by a model in which the surfactant layer is built up by the addition of admicelles to the interface than by a model based on hemimicelles which change structure as surfactant adsorption increases.

As another example, Chandar et al.⁴ report a decrease in the microviscosity experienced by nitroxide spin probes in the adsorbed surfactant layer as the position of the nitroxide group is moved away from the head of amphiphilic probes; this trend is interpreted by the authors to indicate that the aggregate structure is that of a local monolayer. This is not a necessary conclusion, however, since the same dependence has been observed from the same probe molecules in lipid bilayers.⁵ For bilayers such results were interpreted to indicate that the central part of the bilayer, near the ends of the hydrocarbon tails of the lipids, was more fluid than the portion of the bilayer near the headgroups of the lipids, rather than that the surfactant had formed a monolayer.

Chandar et al.⁶ used pyrene and dinaphthylpropane as fluorescence probes of the adsorbed surfactant layer. The pyrene probe appears to interact with adsorbed sodium dodecyl sulfate (SDS) aggregates at the alumina/aqueous electrolyte solution interface from an adsorption density of 410 nm²/molecule to an adsorption density corresponding to 0.25 nm²/molecule. The local polarity of the environment of the probe was found to remain constant, however, from an adsorption density of 310 nm²/molecule to an adsorption density of 0.25 nm²/molecule. In the paper the authors state that "the microenvironment formed by the associated surfactant appears to be similar in nature throughout the

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