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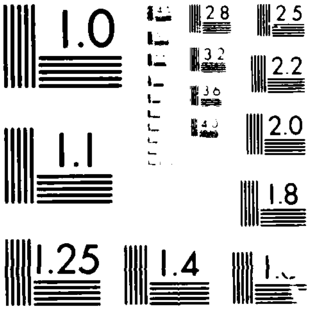

MICROCOPY RESOLUTION TEST CHART

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Adsorption, Mobility and Organization of Organic Molecules at Clay Surfaces probed by Photophysics and Photochemistry

Second Interim Report

15/06/1987

UNITED STATES ARMY

EUROPEAN RESEARCH OFFICE OF THE U.S. NAVY

LONDON, ENGLAND

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Contents

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1 Non-homogeneous distribution of ~~adorbed~~ adsorbed molecules –

In previous studies was observed that cationic detergent molecules form~~ed~~ clusters upon adsorption on a clay surface. The same behaviour has been observed for detergentlike molecules such as the pyrene derivatives, used in our study as molecular probe. For the latter, this non-homogeneous distribution results in ~~gound~~ ground state complexes and a very efficient excimer formation. The photophysical properties of these detergentlike molecules are now used to gain more information about this cluster formation.

Nakamura et al. suggested that surfactant molecules form clusters on a clay surface because of the inhomogeneous negative charge distribution. This means that the adsorption and distribution of the negative sites on the surface.

In our earlier study was suggested that the cluster formation is probably due to a minimalisation of the contact surface between the hydrophobic pyrene derivatives and the surrounding water phase. This sussests that the distribution of adsorbed molecules is certainly also determined by the surrounding medium and not only by the negative sites on the surface.

In order to find out which is the major determinating factor, clay suspensions in different solvents are studied. The clay suspensions in several organic solvents were made as follows: first, the ion-exchange is performed in water because such an ion-exchange is impossible in organic solvents. Therefore the desired amount of Laponite and probe were stirred in 100 ml bidistilled water during several hours. From this suspension the water was removed by drying under vacuo at a temperature of 40 C after which a white dry product was obtained. A portion of this clay sample could then be suspended in the desired organic solvent. After suspending the clay samples in the desired organic solvent, the supernatent has been examined after centrifugation in order to ensure the fact that all pyrene derivatives are adsorbed on the clay surface.

In figure 1 and 2, the fluorescence spectra of a the probe adsorbed on Laponite and suspended in different solvents, are given.

In non-aqueous suspensions, no excimer emission is observed for the probe on Laponite. Since the efficient intermolecular excimer formation in aqueous suspensions has been ascribed to a cluster formation, the absence of excimer emission indicates the absence of clusters on the clay surface when the clay particles are suspended in non-aqueous media. These observations favours the suggestion that the distribution of adsorbed molecules on a clay surface is determined by the surrounding medium and not by the distribution of the negative adsorption sites.

These observations indicate also an appreciable mobility of the adsorbed molecules. Adsorption on the clay surface occurred in an aqueous suspension. The initial distribution is therefore an inhomogeneous one. After resuspending the clay samples in a non-aqueous medium, a redistribution occurs untill a more homogeneous distribution is obtained. Another kind of redistribution was observed in a previous, namely the redistribution between clay particles after adding new clay particles to a suspension. All these observations indicate that the bonding between the positive probe and the negative site on the clay surface is not strong enough to inhibit diffusion of the adsorbed molecules on the clay surface. When a perturbation to a clay suspension is induced, a redistribution of the adsorbed molecules occur untill a new thermodymamically stable situation is obtained.

The fluorescence spectra of the adsorbed pyrene derivatives can also ben used to obtain more information about the orientation of the adsorbed molecules on the clay surface. For 1-substituted pyrene derivatives, the intensity ratio of the monomer fluorescence bands at 378 and 397 nm (I_{378}/I_{397}) is solvent dependent. The I_{378}/I_{397} ratio for the probe adsorbed on the clay and suspended in Methanol is higher than for the probe solubilized in Methanol in absence of clay. These observations favours the suggestion that the pyrene derivatives have a flat orientation on the clay surface. Indeed, when the orientation would be perpendicular, one would expect two similar fluorescence spectra. The difference indicates a more polar environment for the molecules adsorbed on the clay surface.

Another indication for such a flat orientation is found in the time resolved single photon counting analysis of the fluorescence decay of the adsorbed pyrene derivatives. Although,' it is untill now not possible to obtain quantitive information from these analysis, due to the complexity of the fluorescence decay of the adsorbed, qualitive information however can be used to corroborate results obtained from other experiments.

The fluorescence decays of adsorbed pyrene derivatives is characterized by the excistance of short decaytimes in addition to the normal monomer decaytime. Those short decaytimes are probably due to a quenching of the fluorescence by the clay surface. It is indeed generally accepted that iron ions, present in the crystal lattice of the clay can quench the fluorescence of adsorbed molecules.

When the fluorescence decays of the probes in an aqueous and a organic suspension are compared, a considerable increase of the relative contributions of the shorter decay times is observed in organic suspensions. This can be explained by the the assumed flat orientation in organic suspensions. A molecule, lying flat on the surface will be more efficiently quenched by the clay surface compared to a molecule having a perpendicular orientation.

All these observations lead to the conclusion that in non-aqueous media, adsorbed molecules on a clay surface are more or less homogeneous distributed and are lying flat on the clay surface. In aqueous however, hydrophobic interactions results in the formation of clusters on the clay surface.

Influence of the chain length of coadsorbed detergent molecules.

In several studies, the influence of detergent molecules on the photophysical properties of adsorbed probes is reported. In those studies was noticed that the chain length of the detergent molecules information however can be used to corroborate results obtained from other experiments.

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Influence of the chain length of coadsorbed detergent molecules.

In several studies, the influence of detergent molecules on the photophysical properties of adsorbed probes is reported. In those studies was noticed that the chain length of the detergent molecules plays an important role in influencing for example the intermolecular excimer formation of the adsorbed pyrene probes and the quenching of a pyrene derivative by pyridinium ions with various chain lengths. In both cases a so called critical chain length was observed. Detergents with a chain shorter then the critical chain length did not influence the photophysics of adsorbed probes.

Nakamura et al.stated that this is due to a dependence of the geometry of adsorbed detergents on the chainlength. These authors suggested that the detergent molecules with a sufficient chainlength, originally lying flat at the surface, will be orientated perpendicular to the surface when the concentration of detergent is large enough. On the other hand, the shorter detergent molecules remain flat, even at higher concentrations.

In our previous study was suggested that the critical chainlength of the detergent is dependent on the chain length of the probe. For P3N, a chainlength of C_6 was observed. Therefore hexyltrimethylamminium bromide did not influence the photophysics of P3N. In figure 3 the excitation spectra of PN in the presence and absence of hexyltrimethylammonium bromide are given. These spectra indicate the in the presence of this detergent, the ground state interactions of PN dissapears. Contrary to P3N, hexyltrimethylammonium bromide does influence the photophysics of PN.

This proves that the critical chainlength of coadsorbed detergent molecules is correlated with the chainlength

The determinating factor for influencing the distribution of the probe molecules is the ability of the detergent molecules to shield the pyrene chromophore from the waterphase. Then mixed clusters of detergent and probe molecules will be formed. When this shielding cannot be obtained by the coabsorbens, separate clusters of surfactants and probes are formed on the clay surface, resulting in the weaker influence of the detergent molecules on the photophysics of the probe.

These observations also indicate a more or less perpendicular orientation of the molecules adsorbed on the clay surface in an aquous medium. For a flat orientation, the chainlength of the surfactant would not be so critical in influencing the distribution of the probe molecules. This perpendicular orientation is contrary to the flat orientation of the molecules in organic medium. This is probably due to the fact that in aqueous media, the probe molecules are forming clusters, due to an interaction with each other and resulting in a more or less perpendicular orientation. The molecules in fact are forcing each other in a perpendicular orientation. In organic media however, there are no such hydrophobic interactions, resulting in a flat orientation.

3. Influence of the preparation method on the final distribution of the adsorbed molecules

Untill now , our clay samples have been made by adding a concentrated solution of probe to the clay suspensions. This results, as described elsewhere, in a very inhomogeneous distribution of the adsorbed molecules.

When the probe is added in a more diluted way, differences are observed in the fluorescence spectra. The monomer fluorescence band is slightly modified and the excimer emission is much weaker compared to the spectra obtained after adding the same total number of probe molecules as a concentrated solution.

Apparently, the preparation method has an influence on the properties of the adsorbed molecules. The lowered excimer formation efficiency indicates a lower concentration of adsorbed particles on a clay particle. This can be explained in the following way. In our previous report was stated that adsorption of positive molecules on the negatively charged particles is a very rapid process. When the probe is added in a concentrated way, locally there is a very high concentration of probe molecules in the suspension. When these molecules are now rapidly adsorbed on the clay particles in the neighbourhood, this will result in a very high concentration of molecules on these clay particles. These molecules can form clusters to gain a stabilisation, resulting in a very efficient excimer formation.

When however, the molecules are added to the suspension in a more diluted way, the local concentration will never be as high .

In addition, because the volume of the solution to be added is higher, the molecules enter the solution more slowly. These two facts result in lower local concentration of probe molecules on the clay particles. When the local concentration is too low, there is no possibility for the molecules to form the stabilising clusters and this explains the very inefficient excimer formation compared to the previous case. As described in a previous section, when clusters are formed, the molecules are forcing each other in a more or less perpendicular orientation. In absence of those clusters, the molecules are probably orientated flat on the clay surface. This can explain the distortion and the very low fluorescence intensity of the molecules when added in a diluted way to the clay suspension. The fact that in organic media, such a distortion is not observed, can indicate that the interaction between the pyrene chromophore and the clay surface, if no clusters are formed, is stronger in aqueous media compared to organic media.

4. Influence of the structure of the detergent molecules

Untill now, one tailed detergents has been used as coadsorbens. Analogeous experiments as with those one tailed detergents has now been performed with a two tailed detergent, namely didodecyldimethylammonium chloride (DDAC).

For both detergents, the excimer emission decreases with increasing detergent concentration. As described in our previous report this is due to the cluster formation of the detergent molecules on the surface and the preferred solubilisation of the probe in those detergent clusters. The extent of this decrease is however very much different for the two kinds of detergents. For a one tailed detergent, for example cetyltrimethylammomiiun bromide (CTAC), the excimer emission dissapears at a detergent/probe ratio of about 40 . For DDAC the excimer emission becomes zero at a ratio of 15. This large diference can be explained by taking into acount the structural differences of the two kinds of detergent molecules. Due to the two apolar tails, the aggregation number of DDAC clusters will not be as high as for CTAC. This explains the observed difference between the mentioned detergent molecules.

Another interesting feature of those two tailed detergent molecules, is the ability to form a gel after adsorption at the clay particles. An attempt will be made to investigate such gel-like structure with our techniques.

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Figure 1

Fluorescence spectra of a probe adsorbed on Laponite and suspended in water.

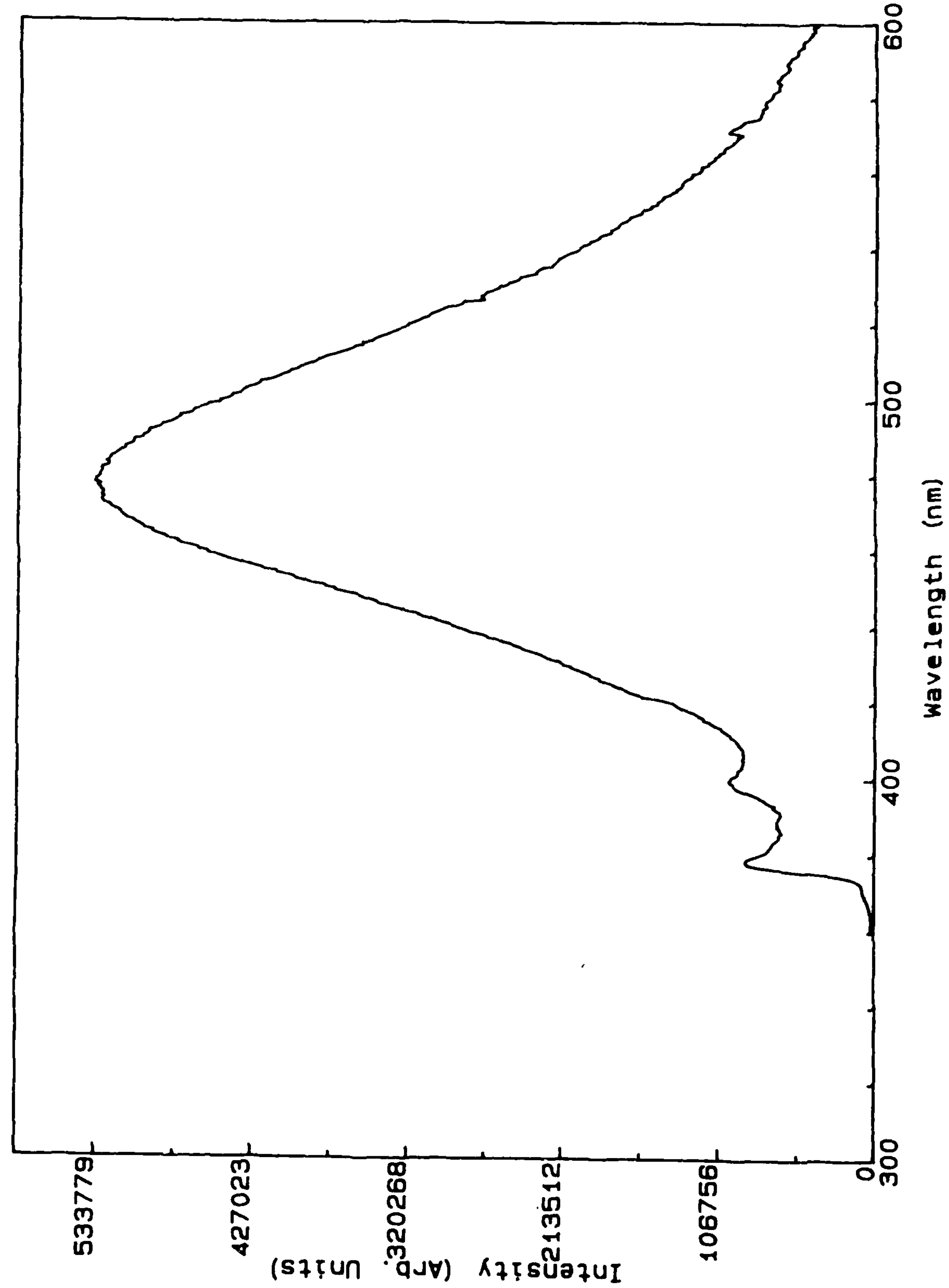


figure 2

Fluorescence spectra of a probe adsorbed on Laponite and suspended in methanol.

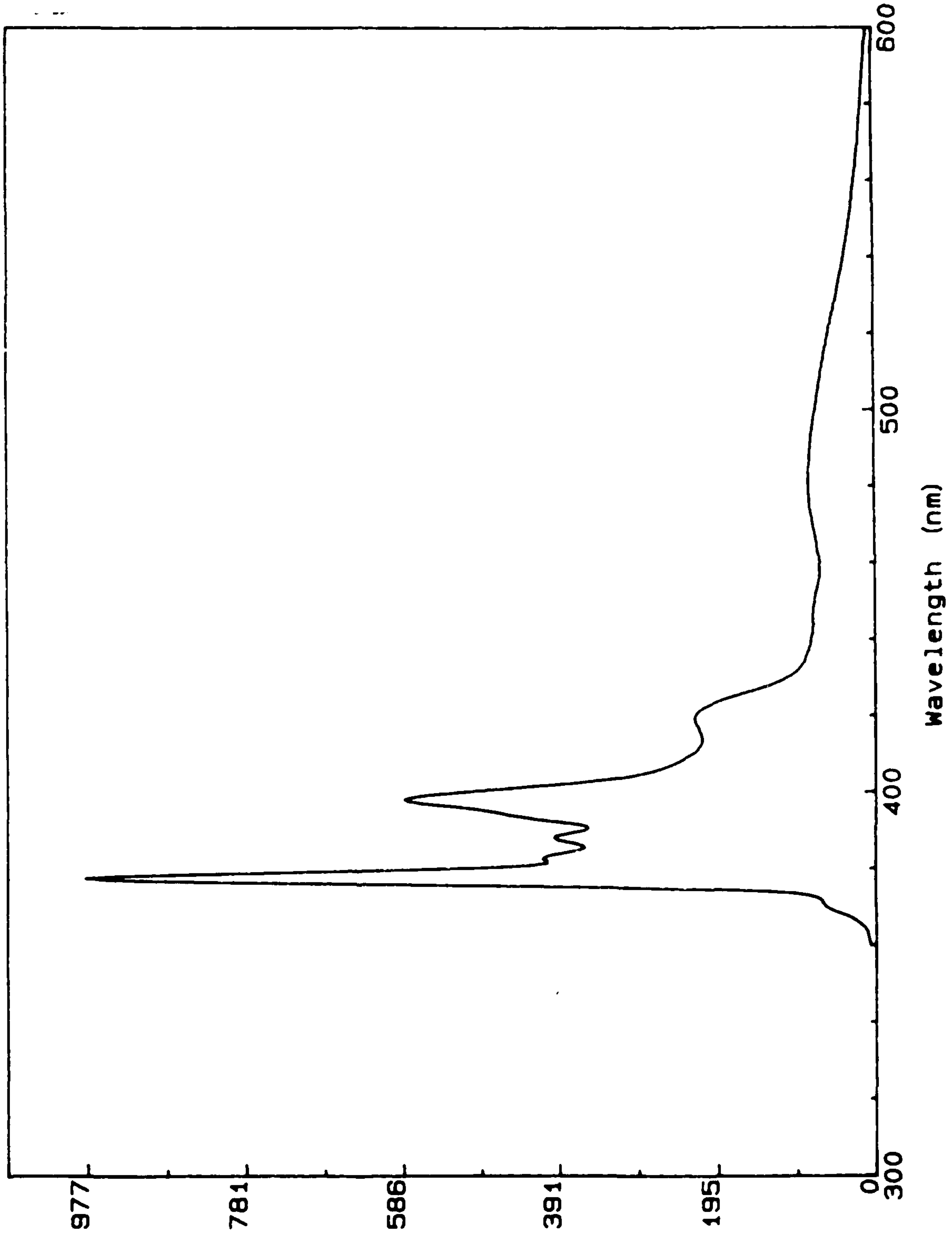
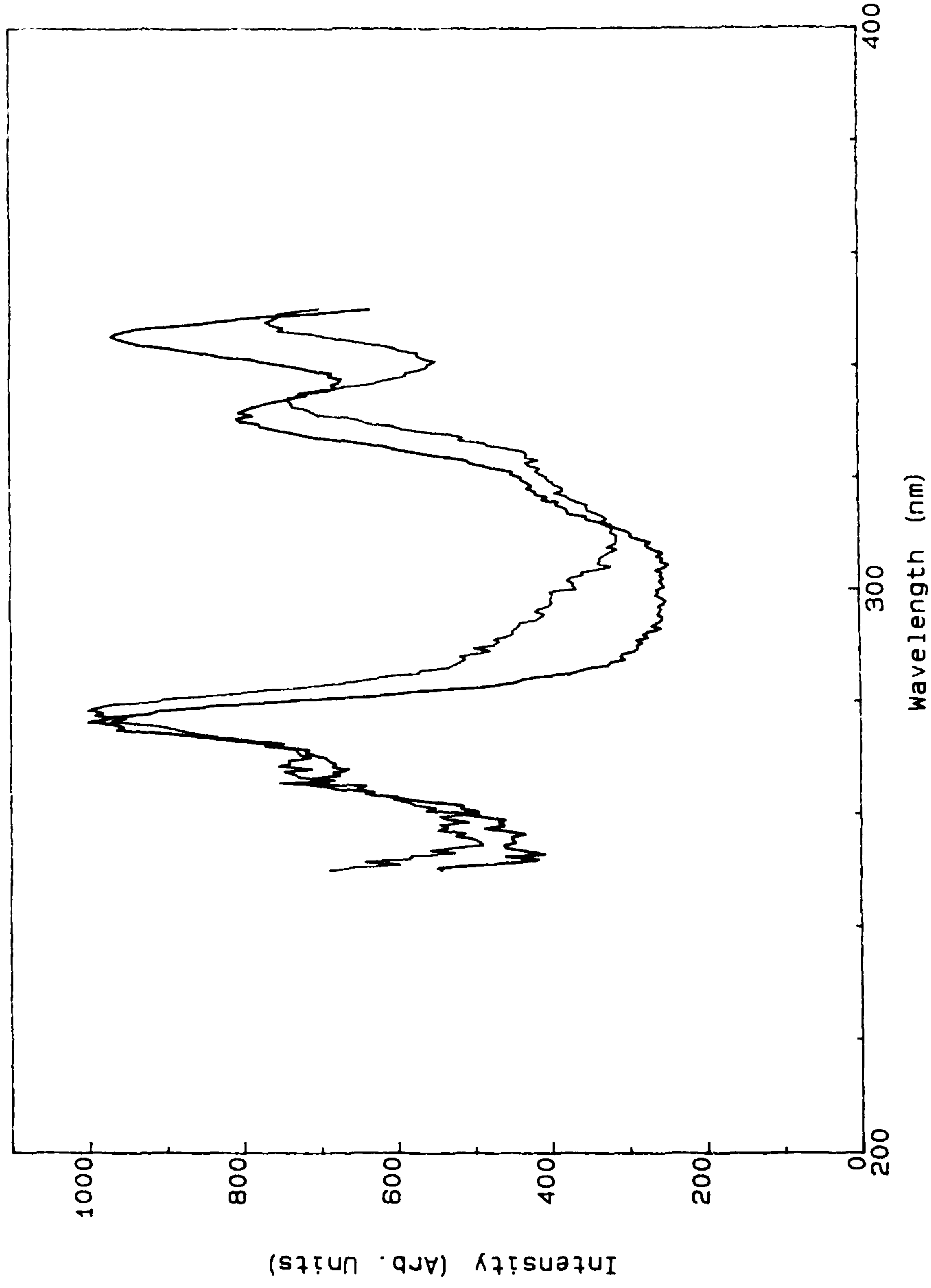


figure 3

excitation spectra of PN with and without hexyltrimethylammonium bromide.



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