Surfactant studies
by Arthur Evans Westwell

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
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Abstract:

An attempt was made to determine the effects on micellization of polar head modifications of decylpyridinium bromide. The differences in aggregation numbers of the surfactants studied are in general not large, and appear to be due more to interactions between polar heads and solvent than to interactions between polar heads.

The ideal optical characteristics of the Brice-Phoenix Differential Refractometer were investigated by means of a computer program and compared to the performance of an actual instrument and the description of its designers It was shown that the possibility of small errors in construction and alignment require an empirical calibration of the instrument rather than the designer's geometrical one, which is approximate at best.

Apparently anomalous results of light scattering by cetylpyridinixim chloride solutions were resolved by demonstrating the adsorption of this compound on glass filters. Unless precautions are taken, the phenomenon can be troublesome in light scattering work with surfactant solutions of low concentration.

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Chemistry

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ABSTRACT

An attempt was made to determine the effects on micellization of polar head modifications of decylpyridinium bromide. The differences in aggregation numbers of the surfactants studied are in general not large, and appear to be due more to interactions between polar heads and solvent than to interactions between polar heads.

The ideal optical characteristics of the Brice-Phoenix Differential Refractometer were investigated by means of a computer program and compared to the performance of an actual instrument and the description of its designers. It was shown that the possibility of small errors in construction and alignment require an empirical calibration of the instrument rather than the designer's geometrical one, which is approximate at best.

Apparently anomalous results of light scattering by cetylpyridinium chloride solutions were resolved by demonstrating the adsorption of this compound on glass filters. Unless precautions are taken, the phenomenon can be troublesome in light scattering work with surfactant solutions of low concentration.

PART I

Ring Substituent Effects on Decylpyridinium Bromide Micellization

INTRODUCTION

The concept of surfactant monomer aggregation in solutions is due to an explanation for the low osmotic activity and relatively high conductivity of soap solutions that was suggested by J. W. McBain in 1913 (1). The idea is now generally accepted that monomers consisting of nonpolar hydrocarbon chains attached to polar groups can aggregate to form colloidal size particles (micelles) in solutions of high enough concentration. If one measures a physical property of such a solution an abrupt change in the property is generally found to occur at what appears to be a characteristic concentration--the critical micelle concentration (CMC). It is probably more accurate to consider the CMC as a narrow concentration range in which the habit of the dissolved surfactant changes from mostly monomer to mostly micelle.

The general structure of the micelle is considered to be a cluster of the hydrocarbon chains with their polar heads exposed to solvent. When the surfactant monomer is ionic, the micelle will be a charged particle whose net charge depends upon association with oppositely charged ions from the solution (counterions). For small micelles, a spherical model seems likely (2-8). When the number of monomers per micelle (aggregation number) is large, the spherical model appears inadequate and other shapes have been suggested such as rods and ellipsoids (6-10).

In the investigations of micelles which have followed McBain's original suggestion, one of the most fruitful techniques for determining aggregation numbers has been that of light scattering. The application of this method to surfactant studies stems from the work of Debye (11, 12), and has been developed to treat multicomponent systems of surfactant and electrolyte by a number of investigators (13-21). In this study aggregation numbers were determined by light scattering and with the equations of Anacker and Westwell (8, 22).

A number of factors that affect surfactant micelle size have been conclusively demonstrated. Aggregation numbers will decrease with a rise in temperature (9, 23), they will increase with increased length of the hydrocarbon chain (9, 23), and they are sensitive to the presence of counterions in solution. Micelle size of ionic surfactants can vary considerably according to the choice of counterion (8, 24), and generally will become larger with increased counterion concentration. In contrast, there seems to be little relationship between aggregation number and ions with the same sign charge as the surfactant monomer (23, 25).

The nature of the polar head has also been recognized as an important factor in micelle formation, but this has not been thoroughly or systematically studied until recently. Other investigations in this laboratory have shown that approach of counterions to the charge center on a variety of ammonium-type polar heads can be sterically hindered by side chains, resulting in smaller micelles (26, 27). These studies have also indicated the importance of polar head-water interactions. Jacobs and Anacker have shown that aggregation numbers of pyridinium ring-decyl chain compounds depend upon the point of attachment of the chain to the ring (28). Micelles are smallest when the chain is on the ring atom bearing the greatest positive charge, and where it can produce the greatest hindrance to the approach of a counterion to that charge.

In addition to the steric and solvent effects, any factor that might enhance the close approach of polar heads would seem to increase the chances for larger micelles. Presumably the presence of counterions does this by helping reduce charge repulsion between neighboring polar heads, but there are several other possibilities.

Another means of reducing charge repulsion between polar heads would be ionization of the polar head to produce an over-all neutral species. Veis and Hoer have made careful measurements of the pH of decyl- and dodecylammonium chloride solutions without added electrolyte (29). The sharp drops in pH observed at the CMC's correspond to the loss of protons from $-NH_3^+$ groups. It is also possible for an alkyl group attached to the 2 or 4 position of a pyridinium ring to lose a proton from the carbon adjacent to the ring (30). If this neutralization effect were important in contributing to micelle formation, a difference in aggregation number might be detected in a series of substituted pyridinium surfactants. Loss of the proton from an -OH group on a cationic polar head is another way in which charge neutralization might be effected.

Hydrogen bonding might be a possible link between polar heads that would promote micelle formation.

Hydrophobic bonding and Van der Waals attraction between alkyl groups on different polar heads have been suggested as factors in micellization (6, 27). These groups, however, could also be sources of steric hindrance.

Stead and Taylor have argued that increased delocalization of charges on polar heads would allow closer approach, and give as an example of this possible effect the lower

CMC's of 1-dodecyl-4-methoxypyridinium bromide and chloride compared to the unsubstituted dodecylpyridinium analogs (32). From measurement of base strengths it is known that alkyl groups can increase the electron density on the pyridine ring (31). Substitution at the 4 position is more effective than at the 3, and the base strength does not change as the group at the 4 position is varied through the series methyl, ethyl, i-propyl and t-butyl. Pyridinium surfactants with alkyl groups at different positions might have aggregation numbers reflecting a difference in charge delocalization. On the other hand, differences in micelle size for a series of alkyl groups at the same position should be due to other causes.

The pyridinium polar head is seen to be a particularly interesting and versatile one for investigation of the effects mentioned above. There is the possibility of various substituents at the different ring positions which might allow detection of steric effects as well as those due to charge delocalization and ionization. The planar structure of the group could also permit closer approach of polar heads than was possible with the ammonium-type surfactants of other comparison studies (26, 27). This might produce a greater sensitivity of aggregation number to some of the factors depending upon polar head interaction.

Since chances of encountering insoluble materials are greater with increased hydrocarbon chain length, surfactants with a decyl group were chosed for this study. They were prepared as bromide salts not only because of the relative ease of preparation, but for the good aggregating power of this ion which was also the counterion of choice.

In addition to the determination of aggregation numbers of twenty different pyridinium-type surfactants, information was also sought from pH measurements, dye solubilization, and calculation of charge distribution on the substituted pyridinium ring.

EXPERIMENTAL

The light scattering measurements were carried out with a Brice-Phoenix Universal Light Scattering Photometer, Series 2000, with an attached chart recorder. Scattering and transmitted intensities were determined as average peak heights for several measurements of a sample, extrapolated back to zero time for the sample in the instrument. This was done because of a general drop of peak height with time, probably due to warming of the solution after it had been placed in the photometer.

All measurements were made with the same cylindrical scattering cell (Brice-Phoenix Catalog no. C-105).

Light of 435.8 nm was used in all determinations. Since one of the compounds studied (decyl 4-cyanopyridinium bromide) was visibly colored and absorbed more strongly at 435.8 nm than at 546.0 nm, scattering measurements were also made for this compound at the latter wavelength. The loss in scattering intensity due to use of a longer wavelength was greater than the intensity loss from absorption at the shorter wavelength, so these results were not used for determining the aggregation number. Instructions for the instrument indicated that no correction was required for measurements of absorbing solutions unless absorption were much greater than that encountered in this case.

The scattering intensities used in the determination of aggregation numbers were measured at 90°. For each sample intensities were also measured at 45° and 135° to check for dissymmetry in the scattered light. Dissymmetry was not detected in any of the samples measured, which meant that the scattering particles were small compared to the wavelength of the incident light.

Samples were prepared by adding weighed amounts of solvent to known weights of surfactant. The solvent consisted of 0.5 molal electrolyte (NaBr, NaCl, HBr, HCl) in water. The water used for these solutions was obtained from reverse osmosis and was then distilled from alkaline permanganate solution. The electrolytes used were reagent grade. A series of solutions for a compound usually consisted of 12 samples ranging from about 3×10^{-3} to 7×10^{-2} molal in surfactant concentration.

The samples were introduced into the scattering cell by filtration through an ultrafine fritted glass filter under nitrogen pressure. Solvent was measured first, and then several samples of the least concentrated surfactant solution were run through the filter until successive samples gave consistent light scattering results (see Part III).

Cell and filter were cleaned beforehand with hot chromic acid solution and rinsed thoroughly with doubly distilled water. The filter was also washed with ammonia solution after treatment with the acid. Absence of dust in the cell was determined from scattering measurements with water taken directly from the still.

Temperature was controlled by keeping the entire room at 25°. Temperature within the photometer would rise 5 to 6 degrees during the series of measurements for one surfactant.

Refractive index measurements were made on unfiltered portions of the same solutions used for light scattering. Only solutions above the critical micelle concentration were measured and compared with the electrolyte solvent. The instrument used was a Brice-Phoenix Differential Refractometer, Model BP-2000-V. Its characteristics are discussed in Part II. The purpose of these measurements was to determine the variation of solution refractive index with surfactant concentration, a quantity required in the calculation of aggregation numbers. In the Brice-Phoenix refractometer this is done by finding the amount of deflection of a slit image that occurs when solutions of different surfactant concentration are compared to solvent in a two section cell.

The relationship of image deflection to refractive index increment for the instrument used was found by empirical calibration. A series of NaCl solutions of accurately known molality was prepared, and the refractive index of each solution was calculated from the refractive index data of Kruis (33). A least squares treatment of Kruis's data gave the following relationship between Δn, the difference between refractive index of solvent and solution, and the NaCl molality (m)

$$\Delta n \times 10^3 = 0.00281 + (10.6203)m - (0.817256)m^2 + (0.155446)m^3$$

This expression was used to calculate the refractive index increment of the NaCl solutions prepared for the instrument calibration. When slit image deflections (Δd) were measured for these solutions, it was apparent that there was not the strict proportional relationship between Δn and Δd that has been claimed by the instrument designers (see Part II). A least squares treatment of the experimental data gave this relationship

$$\Delta n = (9.9737 \times 10^{-4})\Delta d - (1.230 \times 10^{-6})(\Delta d)^2$$

Temperature control for solutions in the refractometer is achieved by circulating water from a constant temperature bath through the metal housing containing the sample cell. After introducing solution into a cell compartment, from 6 to

7 minutes is required for temperature equilibration. A constant reading for the slit image position is not obtained until equilibration has been achieved.

A problem that occurred persistently in the first several series of compounds measured was flow of surfactant solution to the top of the refractometer cell. This appeared to be happening in the corners of the cell compartments, and did not appear to be taking place in the compartment containing solvent. This solution flow seemed to be causing concentration changes either through evaporation at the top of the cell, or by mixing with solvent. When liquid was visible on the top edges of the cell, deflection readings became erratic and inconsistent with prior measurements. This problem was eliminated by removing the cell mounting from the instrument and dipping the top of the cell in melted paraffin. Pressing on the top of the soft wax at the top of the cell with a glass plate produced a smooth flat surface which gave a good seal with the cell cover glass. The paraffin coating prevented solution from reaching the top of the cell.

Each time fresh solution was added to one of the cell compartments the compartment was rinsed several times with the solution to be used.

A Cary Model 14 Recording Spectrophotometer was used in measurements of dye solubilization. The dye used was Orange-OT (OOT), originally prepared by P.T. Jacobs for other investigations (34). For determination of solubilization efficiency, solutions of surfactant in 0.5 m NaBr were prepared as in the light scattering work. To these solutions were added small amounts of OOT in excess of what would ultimately be solubilized. The solutions were sealed in water-tight vials and shaken in a constant temperature bath for five days at 25°. They were then allowed to settle out for two days in the water bath without shaking. Samples for analysis were withdrawn with a hypodermic syringe. In order that all absorption measurements would fall on the same instrument scale, solutions of greater OOT concentration were diluted quantitatively. This was done with a 2% solution of decylpyridinium bromide in 0.5 m NaBr to ensure that all OOT originally solubilized would remain in solution. Spectral scans were made for all samples run, and a maximum absorbance for OOT was found at 498 nm in all cases.

The extinction coefficient was determined for OOT in 2% solutions of various surfactants in 0.5 m NaBr. Small measured amounts of 3.13×10^{-2} molar OOT in acetone were added to weighed amounts of surfactant solutions with a microliter syringe to give OOT solutions of known molality.

Absorbances were measured at 498 nm, which again corresponded to maximum absorbance for all solutions measured.

The pH measurements were made on several sets of solutions of different surfactants above the CMC. The instrument used was a Radiometer pH Meter 4 d with glass and calomel electrodes. Consistent and stable readings were not obtained with the surfactant solutions, possibly due to adsorption of surfactant on the membrane of the glass electrode (see Part III). Another possible source of trouble with these measurements might have been changes in the nature of the surfactant solution due to high chloride ion concentration at the interface with the KCl solution of the calomel electrode.

The compounds used in this study were in general prepared by reacting equimolar amounts of n-decyl bromide and the appropriate substituted pyridine to form substituted decylpyridinium bromide salts. Starting materials that were visibly colored were vacuum distilled before use. Initially these syntheses were carried out by refluxing the two reactants together under a nitrogen atmosphere for 10 to 20 minutes. This usually led to rapid and vigorous reactions and the development of much dark color in the reaction mixture. When the reaction appeared to be complete the mixture was cooled and impure product solidified as a hard waxy mass. Complete solidification could occur in a few minutes at room temperature, overnight in the refrigerator, or could require several weeks of refrigeration. When reactions were carried out in this manner, lower reactivities were apparent for pyridine compounds with substituents in the 2 position.

The products were recrystallized from acetone, ethanol or mixtures of these two solvents. Refrigeration was usually required. In some cases addition of diethyl ether precipitated the product from solution; in other cases addition of ether caused the product to form a separate liquid layer. Recrystallizations were carried out until there was no perceptible color remaining in the product. An exception was the derivative of 4-cyanopyridine, which was bright yellow. The sequence of recrystallizations for some compounds required from 2 to 3 months. The purified products were vacuum dried over P_4O_{10}. Several of the compounds were markedly hygroscopic and subsequent handling of them was done in a nitrogen filled glove bag.

It was found that cleaner products could be obtained if the reactants were dissolved in ethanol and refluxed under nitrogen for 3 to 5 days. After this period, ethanol and excess reactants were removed by vacuum distillation and the product was solidified by cooling. Further treatment of product was carried out as before, but only 5 or 6 recrystallizations were usually required to give a colorless product.

The decylpyridinium bromide monohydrate was from a lot prepared by P. T. Jacobs for a separate investigation (34). The compounds with methanol groups at the 2, 3, and 4 positions of the pyridinium ring were originally made by M. O. Gunsch and were recrystallized and reanalyzed for this investigation. The 3 and 4 methoxymethyl compounds were prepared by P. T. Jacobs for this work.

Composition of the compounds was checked by gravimetric analysis of the bromide content. A summary of the results is given in Table 1 along with a list of symbols used to identify the various surfactants studied.

There were several interesting failures among the attempted syntheses. No reaction could be detected with 2-bromo, 2-cyano, or 2-ethoxypyridine. Reaction with 2-n-propylpyridine yielded a white crystalline product which did not foam in water solution. Bromide analysis and the NMR spectrum suggest that this was 2-n-propylpyridinium hydrobromide. Reaction occurred between decyl bromide and 2-ethanolpyridine to produce a highly viscous material which

TABLE 1

BROMIDE ANALYSIS OF SURFACTANTS

Surfactant	Symbol	%Br Calculated	%Br Found
Decylpyridinium bromide·H_2O	DPB	25.10	25.11
Decyl-2-methylpyridinium bromide	2M	25.42	25.41
Decyl-3-methylpyridinium bromide	3M	25.42	25.47
Decyl-4-methylpyridinium bromide	4M	25.42	25.43
Decyl-2-ethylpyridinium bromide	2E	24.34	24.35
Decyl-3-ethylpyridinium bromide	3E	24.34	24.33
Decyl-4-ethylpyridinium bromide	4E	24.34	24.36
Decyl-2-methanolpyridinium bromide	2MOL	24.19	24.18
Decyl-3-methanolpyridinium bromide	3MOL	24.19	24.19
Decyl-4-methanolpyridinium bromide	4MOL	24.19	24.00
Decyl-3-propanolpyridinium bromide	3POL	22.30	22.28
Decyl-4-propanolpyridinium bromide	4POL	22.30	22.36
Decyl-3-methoxymethylpyridinium bromide	3MOM	23.21	23.20
Decyl-4-methoxymethylpyridinium bromide	4MOM (compound unstable)	23.21	-
Decyl-3-cyanopyridinium bromide	3CN	24.56	24.55
Decyl-4-cyanopyridinium bromide	4CN	24.56	24.52
Decyl-3-bromopyridinium bromide	3BR	21.07	21.10
Decyl-3-hydroxypyridinium bromide	3OH	25.26	25.22
Decyl-4-t-butylpyridinium bromide	4TB	22.42	22.40
Decyl-4-ethanolpyridinium bromide	4EOL	23.21	23.12

resisted all attempts at crystallization. Since direct distillation of this pyridine compound can produce 2-vinylpyridine (35), it is possible that polyvinylpyridine was produced in the reaction. A reaction also occurred between decyl bromide and 2-propanolpyridine. Bromide analysis and investigation by P. T. Jacobs indicated that the product formed had the structure given in Figure 1.

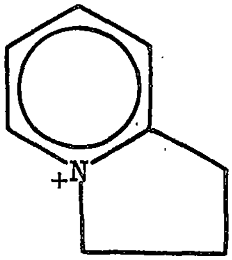

Fig. 1.--Possible Product from 2-propanol Reaction

Reactions with 4-n-propylpyridine and 4-isopropylpyridine appeared to give satisfactory yields of surfactant, but no means were found of recrystallizing and purifying these products for further use.

DISCUSSION

Aggregation numbers for the surfactants studied were calculated from the equations of Anacker and Westwell for surfactant solutions with added electrolyte (8, 22). Scatterin data are treated in accordance with an equation which can be written as

$$Km_2'/R_{90} = A + Bm_2' + \ldots\ldots$$

where

$K = 2\pi^2 n^2 n_2'^2 V^o / L\lambda^4$

$A = 4N\{(2N - fp)^2 + pf^2\}^{-1}$

$B = pA(2m_3)^{-1}\{(1 + p)N^{-1} - A\}$

N = aggregation number

p = effective micellar charge

$f = (\partial n/\partial m_3)_{m_2'} / (\partial n/\partial m_2')_{m_3}$

m_2' = molality of micellar salt (total surfactant molality minus CMC)

R_{90} = Rayleigh ratio at 90° scattering angle ($=3\tau/16\pi$)

n = solution refractive index

$n_2' = (\partial n/\partial m_2')_{m_3}$

m_3 = molality of supporting electrolyte

V^o = volume of solution (cm^3) contining 1 kg water

L = Avogadro number

λ = wavelength (cm) in vacuo of light used

τ = turbidity of solution minus turbidity at CMC

Primed quantities designate molalities in terms of monomer units.

The first equation is based on these assumptions: there is no depolarization of scattered light at 90°; micelles are small compared to λ (there is no dissymmetry); R_{90} represents scattering in excess of that at the CMC; unaggregated surfactant (concentration assumed equal to CMC) can be considered part of the supporting electrolyte.

Equations relating the scattering data to the effective micelle charge and the aggregation number are

$$p = \{2fm_3B + (8m_3B)^{\frac{1}{2}}\}A^{-1}(2 - fA)^{-1}$$

$$N = p(p + 1)A(2m_3B + pA^2)^{-1}$$

If p = 0, N is not calculated from the second equation but from the definition of A. The quantities A and B are determined experimentally as the intercept and slope respectively of a Km_2'/R_{90} vs. m_2' plot and are then used to calculate values of p and N. A computer program is available for performing these calculations. This program calculates the CMC, A^{-1}, N and p for a least squares linear plot of Km_2'/R_{90} vs. m_2'. A^{-1} is an approximation (uncorrected for charge) of the aggregation number.

It was intended that all light scattering work be done with 0.5 m NaBr as solvent, however in some instances chloride rather than bromide solutions were used. This was done either because of insolubility of a surfactant in 0.5 m NaBr (3OH, 4TB), or to allow comparison of aggregating abilities of the bromide-insoluble compounds with those of some of the other surfactants.

When the counterion of the added electrolyte was chloride, the changes of solvent and solute refractive indices with concentration were calculated as described by Anacker and Ghose (8). When calculations were made for a family of isomers the surfactant refractive index gradient used was usually an average of those determined experimentally for the individual compounds. An exception to this was made for the case of the rather different isomers 3MOM and 4EOL where the measured gradients are not very close to the same value. An average was not used for 3MOM and 4MOM since data for 4MOM are not considered very reliable.

Calculated aggregation numbers are given in Tables 2 and 3 along with the CMC's determined from light scattering and from dye solubilization. A key to compound symbols has been given in Table 1. Aggregation numbers in parentheses are not corrected for charge. In some cases only a value uncorrected for charge (A^{-1}) is available. This occurs when

TABLE 2

AGGREGATION NUMBERS OF SURFACTANTS IN 0.5 m NaBr AT 25°

Surfactant	Aggregation Nr.	CMC x 10^3 Scattering	CMC x 10^3 Solubilization
DPB	50 (47 ±0.5)*	11.1	11.2
2M	45 (43 ±0.2)	10.2	10.2
3M	43 (42 ±0.1)	8.9	9.2
4M	45 (43 ±0.2)	8.6	9.3
2E	40 (38 ±0.3)	7.6	8.0
3E	44 (42 ±0.2)	7.0	7.8
4E	43 (42 ±0.3)	6.9	7.6
2MOL	58 (57 ±0.3)	8.9	6.6
3MOL	51 (49 ±0.5)	10.6	8.8
4MOL	52 (49 ±0.2)	9.8	9.0
4EOL	47 (44 ±0.5)	10.2	10.3
3POL	36 (35 ±0.2)	9.0	9.4
4POL	40 (38 ±0.9)	8.8	8.6
3MOM	37 (36 ±0.2)	9.4	9.5
4MOM	(38 ±0.5)	2.0	-
3CN	(50 ±0.5)	10.5	13.0
4CN	(67 ±0.7) (95 ±0.8)	6.2 11.6	- -
3BR	(56 ±0.5)	8.0	8.0

* Values in parentheses are uncorrected for charge. Uncertainties are for least squares determination of A^{-1}.

TABLE 3

AGGREGATION NUMBERS OF SURFACTANTS IN VARIOUS SOLVENTS AT 25°

Surfactant	Aggregation Number	CMC x 10^3 (Scattering)
Solvent = 0.5 m NaCl		
4MOL	(37 ±0.1)*	15.4
3BR	(33 ±0.0)	14.6
4CN	13 (11 ±0.3)	36.0
4TB	36 (34 ±0.4)	7.9
3OH	50 (48 ±0.8)	6.7
Solvent = 0.5 m HBr		
3E	45 (44 ±0.2)	8.2
3MOL	49 (47 ±0.4)	13.5
3POL	35 (34 ±0.4)	12.2
Solvent = 0.5 m HCl		
3OH	(44 ±0.4)	9.8

* Values in parentheses are uncorrected for charge. Uncertainties are for least squares determination of A^{-1}.

the plot of scattering intensity vs. surfactant concentration shows concave upward curvature above the CMC, an effect which is generally believed to result from polydispersity in micelle size and/or an increase in size with concentration (6, 8, 10, 24). The charge-uncorrected values represent lower limits for aggregation numbers, and in most cases where charge-corrected values are available for comparison the uncorrected values are only one or two units lower. A summary of experimental data, and typical data plots, are given in appendix B.

The very different aggregation numbers calculated for two separate determinations of 4CN in 0.5 m NaBr arise from the anomalous behavior of this compound. In a concentration range that appears to start at the CMC, samples of this compound gave markedly higher scattering than was consistent with most of the data for 4CN. Consecutive samples of a single solution in this range , after filtration into the scattering cell, did not produce the same scattering. After two or three different solutions gave these erratic results, subsequent solutions showed the regular and uniform increase of scattering with concentration that is expected for a scattering curve. Unfiltered portions of the oddly behaving solutions showed no anomalies when refractive indices were determined. The phenomenon is specific for 4CN since it occurs with no other compound studied and was very evident in both determinations of 4CN in 0.5 m NaBr, and to a lesser extent in an attempt to determine the aggregation number of 4CN in 0.5 m NaCl. Since the material is known to be adsorbed onto the filter (see Part III), a possible explanation of this behavior is that with solutions above the CMC some of the adsorbed surfactant may be attracted back into solution in micellar form. The disparity in the two aggregation numbers determined for this compound in 0.5 m NaBr can be attributed to the lack of reliable scattering data in the neighborhood of the CMC. It is safe to say only that micelles of 4CN are probably large compared to the rest of those studied in 0.5 m NaBr.

The instability in air of 4MOM and the lack of consistent bromide analyses put the results for this compound in question. There is nothing apparently unusual in the aggregation number, but the value determined for the CMC is notably lower than that for any other compound in the series.

When solutions of 4MOL and 4EOL were prepared, a small amount of insoluble material was visible in the samples of both compounds. After filtration the solutions were clear and the low scattering from samples below the CMC indicated that no colloidal or larger particles were present. This implies that the true surfactant concentrations in these solutions were lower than the calculated values because of an insoluble impurity in the compounds. Calculations for 4EOL on the assumption that true concentrations were 10% less than those originally calculated revised the aggregation number from 47 to 42. The 10% assumption is a considerable exaggeration of the amount of impurity, and a more accurate adjustment of concentrations would probably not reduce the calculated aggregation number by a significant amount. The bromide analyses of the two compounds in question are low, and the differences between the analytical and the calculated precents are larger than for any of the other compounds studied (Table 1). If the analytical results are accurate measures of the amounts of surfactant in these preparations, the percent of impurity would be 0.4% and 0.8% respectively for 4EOL and 4MOL.

The small differences in aggregation numbers accompanying the substitution of different groups on the ring show that the various effects suggested in the Introduction can play only a small role at most in determining micelle size for the compounds studied. This is in contrast to other influences that have been studied by light scattering such as choice and concentration of counterion, length of hydrocarbon tail, and large variations in polar head structure.

The influence of counterion has been investigated by Anacker and Ghose in a study of hexadecylpyridinium bromide (8). For 0.2 m sodium salts of IO_3^-, F^-, Cl^-, BrO_3^- and Br^- as supporting electrolytes, the aggregation numbers were 101, 117, 129, 130 and 2140 respectively. In the present work the dependence upon counterion identity can be seen in the lower aggregation numbers found for 4MOL and 3BR when determined in 0.5 m NaCl as compared to the values for 0.5 m NaBr.

Anacker has shown (5) that the aggregation number of hexadecylpyridinium chloride increases with chloride concentration from a value of 95 in 0.0175 M NaCl to 135 in 0.730 M NaCl.

Aggregation numbers were determined by Jacobs, Geer and Anacker (34) for a series of alkyl pyridinium surfactants with chains of 9 to 14 carbon atoms. The aggregation numbers were 35, 49, 64, 77, 98 and 136 respectively in NaBr solutions.

The extent to which variation in polar head structure can influence micellization can be seen in some of the results of Geer, Eylar and Anacker (26) from decylammonium bromide and some of its derivatives. With no substitution on the ammonium group, the aggregation number in 0.5 m NaBr is 1100. Aggregation numbers for different substitutions were found to be: 670 (methyl), 69 (dimethyl), 48 (trimethyl), 65 (diethyl) and 37 (triethyl).

In comparison to these other results, the differences in micelle size that appear in this study are minute and must be interpreted with caution. It is evident that 3OH has superior aggregating ability compared to the other compounds. Although this compound is not soluble in 0.5 m NaBr, the aggregation number for 3OH in 0.5 m NaCl is substantially larger than that for the compounds that were determined in both solvents. It also seems clear that the presence of an alkyl group leads to a small decrease in size, although it is not clear whether or not the micelle size depends upon the size of the group in going from methyl to ethyl. There is no evidence that the position of such a group on the ring has an effect on aggregation number. The only cases where ring position seems important are with 2MOL which shows a markedly larger size than 3MOL and 4MOL, and with 3CN and 4CN. This latter compound has proved to be highly anomalous in its behavior and is not reliable for making comparisons.

There appears to be a definite trend in aggregation number according to the size of substituents containing -OH groups. If one considers the series 3OH; 2-, 3-, and 4MOL; 4EOL; and 3- and 4POL there is a consistent decrease in aggregating ability. Another relationship that appears associated with the -OH group is seen when comparisons are made between groups of close to the same size. Considering the -OH group to be approximately the same size as $-CH_3$, one can compare hydroxy vs. methyl, and methanol vs. ethyl. In both cases the compounds with -OH groups have the larger micelles. There is also the comparison of 4EOL with its isomers, 3MOM and 4MOM. Again the compound with the hydroxy group is the larger.

There are not enough data from other types of groups to detect trends. A cyano group at the 3 position does not appear to change the aggregation number, while a bromine at this point seems to cause a slight increase. Insolubility of 4TB in 0.5 m NaBr prevents a direct comparison with the other alkyl substituted compounds. Since the aggregation number of 4TB in 0.5 m NaCl is much the same as for 3BR and 4MOL, it appears that this compound is not exceptional in its aggregating ability. The very low and very unreliable aggregation number for 4CN in NaCl solution is another instance of the odd behavior of this compound.

From the determinations of micelle size it is possible to conclude that hydrophobic bonds or Van der Waals forces due to alkyl side chains do not facilitate micelle formation with the compounds studied. Because of the general insensitivity of micelle size to the position of a particular group on the ring, it also appears that steric hindrance of counterion approach is not taking place. The near equality of aggregation numbers for compounds with a group at the 3 or the 4 position indicates that differences in charge delocalization are not great enough to affect micellization of these compounds. The possibilities of polar head neutralization by ionization are discussed below in connection with pH measurements. Of the effects on micelle formation that were suggested in the Introduction, there remains the possibility of hydrogen bonding between -OH groups on adjacent polar heads.

It is tempting to ascribe the relative tendency to large size for hydroxy-containing compounds to this cause. It is difficult, however, to see why this would be more effective for 2MOL than for 3MOL, and why it could be as effective for 4MOL as for 3MOL unless polar heads can easily incline toward one another. The high aggregating ability of 3OH would demand a rather close approach of polar heads if it is dependent upon hydrogen bonding. Hydrogen bonding cannot be ruled out as a factor in the results of this investigation, but it could only account for the tendency to larger size noted, and not for the decrease in size that is connected with the length of the hydrocarbon part of the attached groups.

The extinction coefficient for OOT was found from the slope of a Beer's Law plot for OOT dissolved in 2% solutions of various surfactants in 0.5 m NaBr. The results of these measurements are plotted in Figure 2, and with the exception of the data for 4MOL, all points fall close to a single straight line. A least squares calculation gives the slope of this line as 1.77 x 10^4 kg/mole cm. This is identical to the extinction coefficient determined by Jacobs and Anacker for OOT in a series of decyl surfactants with various non-pyridinium cationic heads (36). The coefficient for OOT in 4MOL solution was found to be 1.57 x 10^4 kg/mole cm. Measurements were made of the absorbance of OOT in several series of surfactant-NaBr solutions saturated with the dye. OOT molalities were calculated with the extinction coefficient values reported above. The slope of a dye molality vs. surfactant molality curve is the solubilization efficiency in terms of moles of dye solubilized per mole of surfactant monomer. These curves appeared linear within experimental