equilibrium concentrations could be calculated from the initial concentrations of A and B. In Figures 4 and 5, $1/\tau_{\mathrm{I}}$ and $1/\tau_{\mathrm{II}}$, respectively, are plotted according to the above equations. From those plots one may derive $k_{12} = (4.8 \pm 0.2)10^9\ M^{-1}\ \mathrm{sec}^{-1}$; $k_{21} = (3.0 \pm 0.2)10^7\ \mathrm{sec}^{-1}$; $K' = 162 \pm 10\ M^{-1}$; $k_{13} = (7.9 \pm 0.2)10^8\ M^{-1}\ \mathrm{sec}^{-1}$; $k_{31} = (1.1 \pm 0.2)\ 10^7\ \mathrm{sec}^{-1}$; $K'' = 70 \pm 5\ M^{-1}$. From these results it may be concluded that the formation of hydrogen-bonded dimers and molecule pairs is very rapid (diffusion controlled at least in the case of the dimerization of ϵ-caprolactam). The pairing takes place in a single step, which means that the second H bond is formed as fast as or faster than the first H bond is broken up again.

The fast pairing reaction is essential for the fast recognition of complementary bases in genetic code reading.

On the other end, the lifetime of the paired complex is very short, *i.e.*, of the order of 10^{-8}–10^{-7} sec. The dissociation involves the breakage of both H bonds. The high dynamic lability, expressed in the short lifetime, is again essential for fast code reading based upon a "trial and error" mechanism, where wrong combinations must disappear rapidly. Since all combinations of two bases will lead to more or less pronounced H-bond pairing, the number of wrong pairs formed and disrupted is large compared to the number of right combinations. The wrong pair, once formed, may not occupy the code site for too long a time. The stability constants must therefore remain relatively low. All these requirements of course do not favor a high accuracy of the molecular code reading process. The accuracy of such processes as they are observed in living organisms cannot be based upon the differential stability of the complementary base pairing alone. A code-checking mechanism presumably involving enzymic recognition sites is required to establish the small error rate observed in the biological processes of genetic information transfer and readout.

Although the base-pairing model systems presented here were studied in nonpolar media, many properties of the actual base-pairing systems in their biochemical environment are conserved. This follows also from kinetic studies with oligonucleotides carried out in aqueous media.[16] The orders of magnitude for the individual H-bond pairing reactions are in the same range. In aqueous media the lifetimes may be smaller because of the competitive H-bond formation with the solvent.

The above example shows that the dielectric relaxation technique described in this paper is very suitable for a study of the rates of base-pairing reactions and yields information which was not obtainable so far. The results of more extensive studies of this type will be published in forthcoming papers.

[16] M. Eigen, G. Maass, W. Müller, and D. Pörschke, to be published.

Counterions and Micelle Size. II. Light Scattering by Solutions of Cetylpyridinium Salts[1]

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Abstract: Dilute solutions of cetylpyridinium bromide in 0.200 *m* NaX (X = F, Cl, Br, ClO_3, BrO_3, IO_3, NO_3) were examined by light scattering. Counterion ability to promote aggregation was found to increase in the order: $IO_3^- < F^- < Cl^-, BrO_3^- \ll Br^- < NO_3^- < ClO_3^- \ll SCN^-, ClO_4^-, I^-$. Micelles associated with the first four anions are probably spheres, while those associated with Br^- are apparently rod-like. Micelles associated with NO_3^- and ClO_3^- are neither rigid rods nor spheres. Cetylpyridinium thiocyanate, perchlorate, and iodide are only slightly soluble in 0.200 *m* NaSCN, $NaClO_4$, and NaI, respectively. The aggregating power of an anion roughly parallels its ability to disrupt the structure of water.

Hartley and coworkers[2,3] concluded from diffusion, conductivity, and transport number measurements that any dependence of micelle size on counterion nature existing in aqueous solutions of cetylpyridinium salts tends to fade out when a large amount of simple salt is added. The results of some recent light-scattering measurements[4] on solutions of dodecyltrimethylammonium salts indicate that counterion specificity can persist at high supporting electrolyte concentrations. These conflicting implications, as well as our rather limited understanding of the counterion's role in micelle formation, prompted the present investigation. We herein report aggregation numbers—as determined by light scattering—of cetylpyridinium micelles present in aqueous solutions of a number of simple sodium salts.

Experimental Section

Most of the solutions examined were prepared by dissolving weighed samples of cetylpyridinium bromide (CPBr) in 0.200 *m* solutions of NaX (X = F, Cl, Br, NO_3, ClO_3, BrO_3, IO_3). All calculations were based on the assumptions that Br^- and X^- are complexed by the micelles in proportion to their respective stoichio-

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[1] A preliminary report was made at the 17th Annual Northwest Regional Meeting of the American Chemical Society in Pullman, Wash., June 1962.

[2] G. S. Hartley and D. F. Runnicles, *Proc. Roy. Soc.* (London), **A168**, 420 (1938).

[3] C. S. Samis and G. S. Hartley, *Trans. Faraday Soc.*, **34**, 1288 (1938).

[4] E. W. Anacker and H. M. Ghose, *J. Phys. Chem.*, **67**, 1713 (1963).

metric concentrations. Except when $X^- = Br^-$, the ratio of X^- to Br^- at the critical micelle concentration (cmc), where scattering data are extrapolated for evaluation, was never less than 75:1. For this reason, aggregation numbers calculated under the assumption that only X^- is complexed by micelles differ little, if at all, from those reported here.

Scattering data were treated in accordance with one of several equations developed earlier[5] for surfactant solutions containing added electrolyte. It can be written as

$$Km_2'/R_{90} = A + Bm_2' + \cdots \quad (1)$$

where

$$K = 2\pi^2 n^2 (\mathrm{d}n/\mathrm{d}m_2')_{m_3}{}^2 V^\circ / L\lambda^4 \quad (2)$$

$$A = 4N[(2N - fp)^2 + pf^2]^{-1} \quad (3)$$

$$B = pA(2m_3)^{-1}[(1 + p)N^{-1} - A] \quad (4)$$

The symbols in these expressions have the following meanings: m_2' is the molality of the micellar salt (primes refer to quantities in terms of monomer units), *i.e.*, total molality of surfactant minus the cmc; R_{90} is Rayleigh's ratio for a 90° scattering angle; n is the solution refractive index; m_3 is the molality of supporting electrolyte; V° is the volume of solution containing 1 kg of water; L is Avogadro's number; λ is the wavelength under vacuum of the light used; N is the micellar aggregation number, *i.e.*, the number of surfactant ions per micelle; p is the effective micellar charge; and $f = (\mathrm{d}n/\mathrm{d}m_3)_{m_2'}/(\mathrm{d}n/\mathrm{d}m_2')_{m_3}$.

A and B are experimentally determined quantities, being respectively the intercept and limiting slope of the Km_2'/R_{90} *vs.* m_2' plot. Expressions suitable for evaluating p and N are obtained by solving eq 3 and 4 simultaneously. The result is

$$p = [-2fm_3B \pm (8m_3B)^{1/2}]A^{-1}(fA - 2)^{-1} \quad (5)$$

$$N = p(p + 1)A(2m_3B + pA^2)^{-1} \quad (6)$$

If B is 0, $p = 0$ and $N = A^{-1}$.

Equation 1 is based on the following assumptions: there is no depolarization of the scattered light at 90°; the micelles are small compared to λ (*i.e.*, there is no dissymmetry); R_{90} represents the scattering of a solution in excess of that at the cmc; and unmicellized surfactant, concentration assumed equal to that of the cmc, can be lumped in with the supporting electrolyte.

When two different counterions coexist in solution, measured refractive index gradients of surfactant and supporting electrolyte must be corrected to reflect this situation. Thus, if one has a solution a molal in NaX and b molal in CPBr, one regards the supporting electrolyte as $Na_{a/(a+cmc)}(CP)_{cmc/(a+cmc)}X_{a/(a+b)}Br_{b/(a+b)}$ of molality $m_3 = a + \mathrm{cmc}$ and the solute as $CPX_{a/(a+b)}Br_{b/(a+b)}$ of molality $m_2' = b - \mathrm{cmc}$. One can approximate the refractive index gradients of supporting electrolyte and solute by

$$(a + \mathrm{cmc})^{-1}(a + b)^{-1}[a^2(\mathrm{d}n/\mathrm{d}m_{\mathrm{NaX}}) + ab(\mathrm{d}n/\mathrm{d}m_{\mathrm{NaBr}}) + a(\mathrm{cmc})(\mathrm{d}n/\mathrm{d}m_{\mathrm{CPX}}) + b(\mathrm{cmc})(\mathrm{d}n/\mathrm{d}m_{\mathrm{CPBr}})]$$

and

$$(a + b)^{-1}[a(\mathrm{d}n/\mathrm{d}m_{\mathrm{CPX}}) + b(\mathrm{d}n/\mathrm{d}m_{\mathrm{CPBr}})]$$

respectively.

The computational procedure for a determination can be simplified somewhat by working with a m_2'/R_{90} *vs.* m_2' plot in place of a plot involving Km_2'/R_{90}. One then need calculate but a single K, that appropriate at the cmc, and apply it to the intercept and limiting slope to get the A and B required for the computation of p and N with eq 5 and 6.

Instrumentation. The initial measurements at supporting electrolyte concentration levels of 0.1 M[1] and 0.200 m were made some years ago in a locally constructed photometer, which has been described elsewhere.[4] Since the photomultipler tube in this instrument can only accept light scattered at 90°, it could not be used to measure the dissymmetry which existed in several of the systems investigated. Recently, a Brice-Phoenix photometer became available and was used to repeat all of the original work at the 0.200 m supporting electrolyte concentration level. In addition, dissymmetry measurements were made when appropriate. A cylindrical cell, Catalog C105, was employed for measurements at scattering angles of 45, 90, and 135°. A dilute solution of fluorescein was used to check alignment of the cell in the photometer and for stray radiation at scattering angles of interest. The 90° photometer was calibrated with 0.5% Cornell polystyrene in toluene,[6-8] appropriate scattering volume and refractive index corrections being made. The Brice-Phoenix photometer was calibrated with the aid of the opal glass diffuser provided by the manufacturer. A comparison of similar runs on the two instruments indicated that the calibrations were in at least 95% agreement. Only data obtained with the commercial photometer are reported here.

Refractive index measurements were made in a differential refractometer constructed for an earlier investigation.[9]

Light of wavelength 4358 Å was employed and measurements were made at temperatures close to 35°.

Materials. CPBr was prepared by refluxing 200 ml of reagent grade pyridine with 118 g of redistilled 1-bromohexadecane (bp 145° at *ca.* 1 mm) for 4 hr. The crude material obtained on cooling was recrystallized repeatedly from water and a variety of mixtures. These included ethanol–acetone, water–acetone, and ethanol–ether. After vacuum desiccation and storage over P_4O_{10}, the purified surfactant was analyzed for bromine. *Anal.* Calcd for $C_{21}H_{38}BrN$: Br, 20.79. Found: Br, 20.87.

CPCl was prepared by dissolving CPBr in a hot concentrated solution of NaCl. The product obtained on cooling was recrystallized twice from concentrated NaCl solutions and then three times from water–acetone mixtures. The final crop of crystals was air-dried and analyzed for chlorine and water. *Anal.* Calcd for $C_{21}H_{38}ClN \cdot H_2O$: Cl, 9.90; H_2O, 5.03. Found: Cl, 10.08; H_2O, 3.4. The crystals were assumed to have the composition $C_{21}H_{38}ClN \cdot 0.655H_2O$, which is based on the chloride analysis, the more precise of the two.

Inorganic salts were of reagent grade and oven dried before use.

Water used in solution preparation was doubly distilled, the second distillation being from alkaline permanganate.

All solutions were prepared by weight and filtered under nitrogen pressure through an ultrafine, fritted Pyrex glass funnel directly into the scattering cell.

Results and Discussion

Measured refractive index gradients, $(\mathrm{d}n/\mathrm{d}m_{\mathrm{CPBr}})_{0.2\,m\,\mathrm{NaX}}$, and computed refractive index gradients, $(\mathrm{d}n/\mathrm{d}m_{\mathrm{CPX}})_{0.2\,m\,\mathrm{NaX}}$, are presented in Table I.

Table I. Concentration Gradients of the Refractive Index at 4358 Å and ~35°

X	$(\mathrm{d}n/\mathrm{d}m_{\mathrm{CPBr}})_{0.2m\mathrm{NaX}}$, kg/mole	$(\mathrm{d}n/\mathrm{d}m_{\mathrm{CPX}})_{0.2m\mathrm{NaX}}$, kg/mole
F	0.0650	0.0558
Cl	0.0646	0.0603
Br	0.0647	0.0647
NO_3	0.0636	0.0586
ClO_3	0.0634	0.0588
BrO_3	0.0627	0.0645
IO_3	0.0623	0.0736

In the computational procedure, surfactant solutions were considered to be mixtures of CPX, NaX, and NaBr. Thus, a solution a molal in NaX and b molal in CPBr was treated as being b molal in CPX, b molal in NaBr, and $(a - b)$ molal in NaX. A measured refractive index difference between a surfactant solution and the solvent, 0.200 m NaX, was corrected for the difference in NaX and NaBr concentrations by adding the quantity $b(\mathrm{d}n/\mathrm{d}m_{\mathrm{NaX}} - \mathrm{d}n/\mathrm{d}m_{\mathrm{NaBr}})$. The gradients $\mathrm{d}n/\mathrm{d}m_{\mathrm{NaX}}$

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(5) E. W. Anacker and A. E. Westwell, *J. Phys. Chem.*, **68**, 3490 (1964). The factor in brackets in the first term on the right-hand side of eq 12 in this paper should be squared. The parenthesis immediately preceding z' should be removed and placed between $m_2'^*$ and dn.

(6) B. A. Brice, M. Halwer, and R. Speiser, *J. Opt. Soc. Am.*, **40**, 768 (1950).

(7) P. Doty and R. F. Steiner, *J. Chem. Phys.*, **18**, 1211 (1950).

(8) C. I. Carr, Jr., and B. H. Zimm, *ibid.*, **18**, 1616 (1950).

(9) E. W. Anacker, *J. Colloid Sci.*, **8**, 402 (1953).

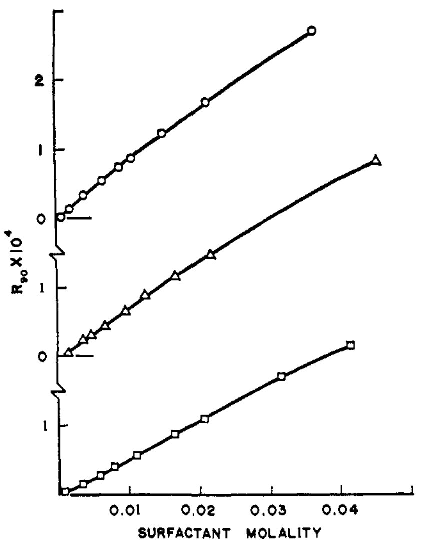

Figure 1. Scattering at 90° by solutions of CPBr which are 0.200 m in NaF (□), $NaIO_3$ (△), and $NaBrO_3$ (○).

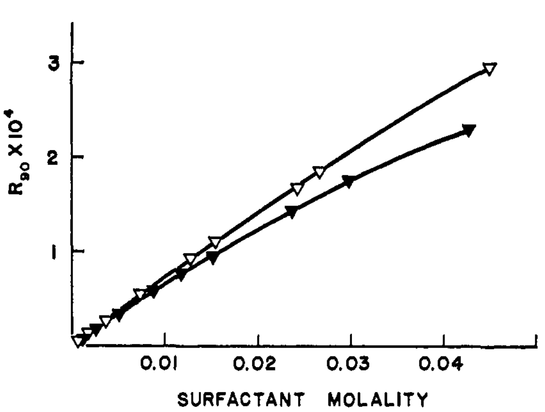

Figure 2. Scattering at 90° by solutions of CPCl (▼) and CPBr (▽) which are 0.200 m in NaCl.

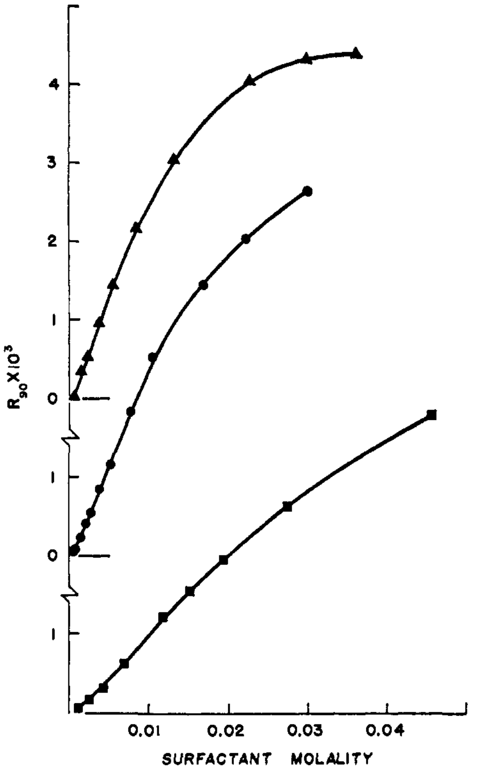

Figure 3. Scattering at 90° by solutions of CPBr which are 0.200 m in NaBr (■), $NaNO_3$ (●), and $NaClO_3$ (▲).

were obtained in another investigation.[4] Within experimental error, refractive index *vs.* surfactant molality plots were linear over the ranges of interest and gradients could be equated to slopes.

The 90° scattering data collected in the various determinations are plotted in Figures 1–3. Solvent scattering has been subtracted in each case. Concave-upward curvature at low surfactant concentrations is present in some of the plots. This behavior sometimes indicates the presence of an impurity which is solubilized when the surfactant concentration is raised. It could also be the consequence of a rather strong dependence of micelle size distribution on surfactant concentration. We lean away from the first possibility because the curvature is absent in some cases (CPBr in NaCl, CPBr in $NaBrO_3$, and CPCl in NaCl) and, when it exists, is reminiscent of the curvatures in similar plots for other surfactants[4,10] which were apparently quite pure. In any event, the curvatures precluded accurate cmc assignments. The m_0 values reported in Table II are in reality only intersections of the concentration axis and analytic extensions of those portions of the scattering curves lying above surfactant molalities of *ca.* 0.004. Extrapolations were made through the application of a least-squares procedure similar to one previously described.[9,11] In addition to yielding an A and B for the best linear plot of Km_2'/R_{90} *vs.* m_2', the procedure provides an m_0, a somewhat idealistic cmc, required for establishing definite values for m_2'. The quantity m_0 is idealistic in the sense that it represents the cmc that would be found if the micelle size distribution present at high surfactant concentration was preserved on dilution, if no micelles existed below the cmc, and if the concentration of monomeric surfactant in the presence of micelles was equal always to the cmc.

Table II. Micellar Aggregation Numbers for CPBr in 0.200 m NaX

X	$10^4 m_0$, moles/kg	$1/A$[b]	N	$10^3 B$	p'
IO_3	12	95	101	83.0	0.18
F	11	116	117	24.6	0.10
Cl[a]	2.6	123	126	68.0	0.16
Cl	0.65	127	129	28.2	0.11
BrO_3	1.8	126	130	39.7	0.12
Br	24	2,110	2,140[c]	7.30	0.054[d]
NO_3	20	7,780	7,850[c]	7.68	0.055[d]
ClO_3	26	11,300	11,400[c]	10.2	0.064[d]
I			Precipitation		
ClO_4			Precipitation		
SCN			Precipitation		

[a] CPCl was the solute. In the run represented by the next line, CPBr was the solute. [b] Aggregation number corresponding to p = 0. [c] Not corrected for dissymmetry. See text for discussion. [d] Based on aggregation numbers uncorrected for dissymmetry.

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(10) P. Debye and E. W. Anacker, *J. Phys. Colloid Chem.*, **55**, 644 (1951).

(11) For corrections to least-squares equations in ref 9, see Errata, *J. Colloid Sci.*, **9**, 88 (1954).

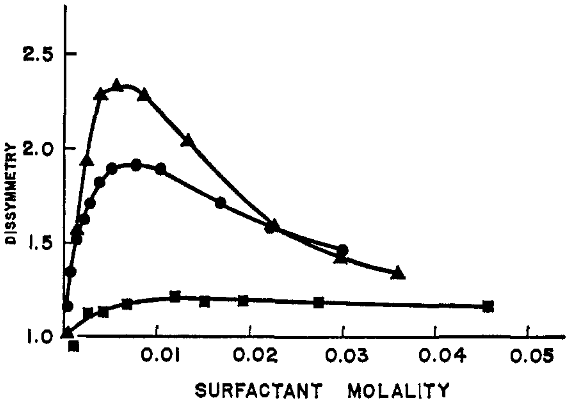

Figure 4. Dissymmetry (scattered intensity at 45° divided by scattered intensity at 135°) exhibited by CPB solutions which are 0.200 *m* in NaBr (■), $NaNO_3$ (●), and $NaClO_3$ (▲). Correction for reflection effects has been made according to the recommendations of Y. Tomimatsu and K. J. Palmer, *J. Phys. Chem.*, **67**, 1720 (1963).

It is doubtful that the m_0 values reported in Table II will correlate well with the cmc's that might be found by other methods.

Light scattered from solutions covered by Figures 1 and 2 (X = F, IO_3, BrO_3, Cl) showed little if any dissymmetry. This behavior is consistent with the relatively small aggregation numbers found and reported in Table II. Although some counterion specificity is apparent, all aggregation numbers are fairly close to the value which might be assigned to a fully developed spherical micelle.

Comparison of the aggregation numbers in Table II for the CPBr and CPCl runs in 0.200 *m* NaCl (Figure 2) indicates that the procedure followed here, *i.e.*, using the surfactant CPBr in NaX solution to estimate the aggregation number of CPX, is a practical one. The difference in the p' ($p' = p/N$) values possibly reflects a preference of cetylpyridinium micelles for bromide over chloride ions. This cannot be stated unequivocally, however, as p is only an *effective* charge, based on the assumption that all activity coefficients are constant. In principle, aggregation numbers are also only *effective*. However, relatively large variations in p are accompanied by much smaller percentage changes in N. Thus, there is some reason to feel that N's are better approximations to actual aggregation numbers than p's are to actual micellar charges. In any event, because of the continuously changing ratio of the two anions in the CPBr in 0.200 *m* NaCl run, the slope of the Km_2'/R_{90} *vs.* m_2' plot is probably dependent on m_2'. That used to calculate p' is representative of the entire surfactant concentration range from which data were taken. A slope derived from accurate data at the low end of the concentration range would probably yield a p' in closer agreement with that obtained for the CPCl in the 0.200 *m* NaCl run. There was not enough accurate data at low surfactant concentrations to check this, however.

The solutions providing data for Figure 3 (X = Br, NO_3, ClO_3) exhibited appreciable dissymmetry, as shown in Figure 4. The dissymmetry *vs.* surfactant molality plot corresponding to X = Br is very similar to one obtained a number of years ago for cetyltrimethylammonium bromide–potassium bromide–water mixtures.[10] Application of the reasoning used in the earlier investigation leads to a similar conclusion: a rod is a better model for cetylpyridinium bromide micelles than is a sphere. The Z^{-1} (Z is the ratio of the intensity of the light scattered at an angle of 45° to that scattered at 135°) *vs.* CPBr molality plot is linear above the cmc and yields an intrinsic dissymmetry of 1.22. This corresponds[12] to a rigid rod length of 854 Å. The number of cetyl chains in a cylinder 854 Å long, 42.1 Å (twice the length of an extended cetyl chain) in diameter, and of density 0.775 g/ml (density of liquid cetane) is 2460. The experimental aggregation number corrected for dissymmetry (assuming a rod-like micelle) is 2480. The agreement, which is better than one could reasonably expect, is strong evidence for rod-like CPBr micelles in 0.200 *m* NaBr. Spheres are readily discounted since an intrinsic dissymmetry of 1.22 corresponds to a sphere radius of 300 Å, which is more than 14 times the length of the extended cetyl chain, and an aggregation number of *ca.* 137,000, which is more than 55 times larger than the experimental value after correction for dissymmetry.

Unless its radius is considerably shorter than the length of the extended cetyl chain, the rigid rod is not a good model for the micelles present in CPBr–$NaNO_3$ (0.200 *m*)–H_2O and in CPBr–$NaClO_3$ (0.200 *m*)–H_2O mixtures. The maximum observed dissymmetries correspond to rods having aggregation numbers 2.6 (X = NO_3) and 3.6 (X = ClO_3) times larger than the dissymmetry corrected experimental aggregation numbers. If intrinsic rather than maximum dissymmetries had been used in the calculations, larger factors of disagreement would have been obtained. Spheres are also poor models. For X = NO_3, the aggregation number calculated on the basis of a spherical model for the micelle is some 67 times larger than the observed aggregation number which has been corrected for dissymmetry. It is possible that a flexible rod is a reasonable micellar model for the systems under discussion. Stigter[13] has had some success in treating the viscosity data of Kushner, Hubbard, and Parker[14] for micelles of dodecylammonium chloride in aqueous sodium chloride solutions on this basis.

An attempt was made to determine micellar aggregation numbers in 0.200 *m* solutions of NaI, NaSCN, and $NaClO_3$. This was not possible at 35°, however, since precipitation occurred when CPBr and solutions of these salts were mixed.

It is probably significant that there are two distinct groups of aggregation numbers in Table II, one corresponding to values in the 101–130 range and one corresponding to values which exceed 2000. It seems likely that micelles in the first group are spheres. If this is the case, the aggregation number has a geometrically determined upper limit. The radius of a spherical cetylpyridinium micelle cannot be too much greater than the length of an extended cetyl chain, assuming that the polar heads of the aggregated surfactant ions must lie in the micelle–water interface. Furthermore, the density of the hydrocarbon interior cannot too greatly exceed that of liquid cetane. Once the maximum size is achieved, substitution of one

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[12] For tables relating dissymmetries, particle scattering factors, and characteristic dimensions of rigid rods and spheres, see ref 7.

[13] D. Stigter, *J. Phys. Chem.*, **70**, 1323 (1966).

[14] L. M. Kushner, W. D. Hubbard, and R. A. Parker, *J. Res. Natl. Bur. Std.*, **59**, 113 (1957).

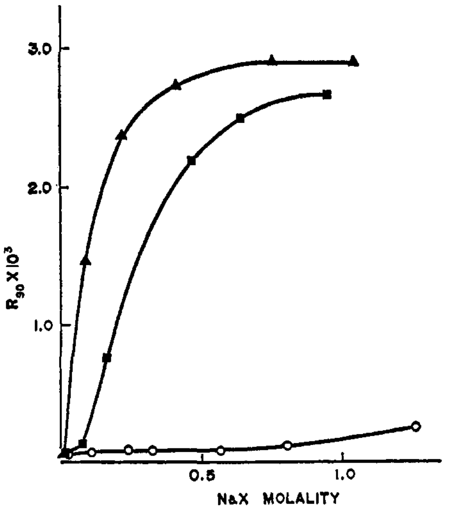

Figure 5. Scattering at 90° by solutions with a constant CPBr concentration (0.0100 *m*) and variable NaX concentration: ○, X = BrO_3; ■, X = Br; ▲, X = ClO_3.

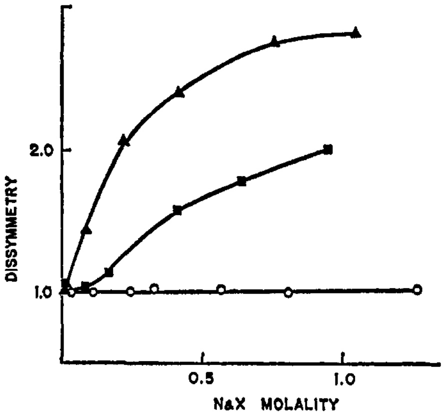

Figure 6. Dissymmetry exhibited by solutions with a constant CPBr concentration (0.0100 *m*) and variable NaX concentration: ○, X = BrO_3; ■, X = Br; ▲, X = ClO_3. Dissymmetry has been corrected for reflection effects.

counterion for another and increasing the supporting electrolyte concentration will have no effect on the aggregation number of the spherical micelle. Some support for this viewpoint comes from an earlier light-scattering study[15] of CPCl–NaCl–H_2O mixtures. For a rather broad range of sodium chloride concentrations above *ca.* 0.3 *M*, CPCl micelles appear to have an essentially constant aggregation number of *ca.* 136. Since the radius of a liquid droplet of cetane containing 136 molecules and possessing a density of 0.775 g/ml is 25 Å, *i.e.*, only a few angstroms greater than the length of an extended cetyl chain, there is a strong inference that the CPCl micelles are spheres and retain this shape through a rather broad sodium chloride concentration range. It is also important to note that Ford, Ottewill, Parreira[16] found that the micellar weights of dodecylpyridinium chloride and dodecylpyridinium bromide remained virtually constant over a wide range of supporting electrolyte concentrations. The two essentially constant aggregation numbers, however, were not in close agreement, as the reasoning given above would seem to demand. Part of the trouble may lie in the use of incorrect refractive index gradients in the calculation of micellar weights. Ford, *et al.*, used light of wavelength 5461 Å in their light-scattering measurements and light of a different wavelength, 5600 Å, for measuring refractive index gradients. It also seems peculiar that the gradient for dodecylpyridinium bromide is reported to be less than gradients for the chloride and iodide. One would expect it to be in between.

If at some supporting electrolyte concentration the micelle is able to abandon its spherical conformation and assume another shape, the aggregation number may again become strongly dependent on the supporting electrolyte strength. This is probably what has happened for the micelles of the second group in Table II, *i.e.*, those with aggregation numbers exceeding 2000. To test this possibility, several runs were made in which the CPBr concentration was held constant at 0.01 *m* and the NaX concentration allowed to vary. The 90° scattering and dissymmetry data collected are shown in Figures 5 and 6. They strongly suggest that $CPBrO_3$ micelles are spherical and remain so up to a $NaBrO_3$ concentration of *ca.* 0.6 *m*. If CPBr micelles are spherical in any NaBr concentration range, it is undoubtedly below 0.1 *m*. Above this level, they must certainly have some other shape. The $NaClO_3$ concentration range which supports spherical $CPClO_3$ micelles is either extremely narrow or nonexistent.

When applied to the ions Cl^-, IO_3^-, F^-, and BrO_3^-, Hartley's conclusion that dependence of cetylpyridinium micelle size on counterion nature tends to vanish in the presence of large amounts of simple salts is probably a valid one. It does not hold, however, when the counterions I^-, SCN^-, ClO_4^-, ClO_3^-, NO_3^-, and Br^- are included.

It is perhaps worth commenting that solutions of CPBr containing NaBr, $NaClO_3$, or $NaNO_3$ are visibly turbid and stable over rather large supporting electrolyte concentrations. This observation stands against the possibility raised by Kushner and Hubbard[17] that dissymmetry measurements made some years ago with cetyltrimethylammonium bromide–potassium bromide–water mixtures[10] involved crystallites of detergent rather than micelles since the "...measurements were made so close to the salting out region...." The present results demonstrate that opalescence and high dissymmetry do not necessarily portend imminent crystallization.

When the anions studied in this investigation are arranged in order of increasing aggregating power, a sequence is obtained which is very similar to that found in the work with dodecyltrimethylammonium micelles.[4] As was pointed out then, the order is roughly the same as Bruins' lyotropic series of anions.[18] Some alterations in order in the series may accompany changes in concentration or phenomena. There have been other studies[3,16,19–24] of anion influence on the properties of cationic surfactants. Although each of these studies

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(15) E. W. Anacker, *J. Phys. Chem.*, **62**, 41 (1958).

(16) W. P. J. Ford, R. H. Ottewill, and H. C. Parreira, *J. Colloid Interface Sci.*, **21**, 522 (1966).

(17) L. M. Kushner and W. D. Hubbard, *J. Colloid Sci.*, **10**, 428 (1955).

(18) E. M. Bruins, *Proc. Acad. Sci. Amsterdam*, **35**, 107 (1932).

(19) H. Lange, *Kolloid-Z.*, **121**, 66 (1951).

(20) K. Meguro and T. Kondo, *Nippon Kagaku Zasshi*, **80**, 818 (1959).

(21) I. Cohen and T. Vassiliades, *J. Phys. Chem.*, **65**, 1774 (1961).

(22) K. W. Herrmann, *ibid.*, **68**, 1540 (1964).

(23) P. Mukerjee and A. Ray, *ibid.*, **70**, 2150 (1966).

(24) M. F. Emerson and A. Holtzer, *ibid.*, **71**, 1898 (1967).

has usually involved only a rather limited number of counterions, the observed effects adhere closely to Bruins' series.

A number of factors[4] seem to be responsible for lyotropic effects, and it is unlikely that a quantitative explanation in terms of any single property is possible. Nevertheless, it is interesting to compare the anion order established here on the basis of aggregating power with the order based on water-structure disrupting ability. This comparison is pertinent in view of the current feeling that micelle formation is an entropy-directed process and is influenced by changes in the water structure surrounding surfactant ions.[25–30]

At least three different quantities have been employed as measures of the ability of an ion to alter the structure of water. Bingham[31] used equivalent ionic fluidity elevations. Frank and Evans[32] introduced ΔS^{st}, supposedly representing the extra entropy of vaporization due to the effect of the ions in the structure of the solution. Gurney[33] and Kaminsky[34] used the "viscosity-B-coefficient" in the expression of Jones and Dole[35] for the relative viscosity of solutions of strong electrolytes. The available literature values for these quantities are given in Table III for the anions studied in this investigation. Negative values of B and ΔS^{st} and positive values of the equivalent ionic fluidity elevation, Δ, imply a structure-breaking ability. Values of opposite sign indicate a structure-promoting tendency. Examination of the table suggests that there is some coupling between the aggregating power of an anion and its structure-breaking ability. Such a relationship could not be linear.

Table III. Structure-Breaking Ability of Anions (25°)

Anion[a]	Δ,[b] rhes	B,[c] l./mole	ΔS^{st},[d] eu
IO_3^-	−12.5	0.140	
F^-	−13.6		3.5
Cl^-	0.28	−0.0070	−10.2
BrO_3^-	−0.8	0.0062	
Br^-	3.09	−0.042	−13.9
NO_3^-	3.06	−0.0460	−19.4
ClO_3^-	0.87	−0.0240	
SCN^-	3.09		
ClO_4^-	7.4		
I^-	7.58	−0.0685	−17.9

[a] In order of increasing aggregating power. The Cl^- and BrO_3^- ions are essentially equivalent. The order for SCN^-, ClO_4^-, and I^- could not be established in this investigation because of precipitation. According to previous work (see ref 4), SCN^- should come before ClO_4^- and I^-. [b] Equivalent fluidity elevation. Values taken from ref 31; rhe = poise^{-1}. [c] Viscosity-B-coefficient. Values taken from ref 34. [d] Values taken from ref 32. ΔS^{st} represents the extra entropy of vaporization due to the effect of the ions in the structure of the solution.

If one chooses to speculate on the nature of the coupling between a counterion's aggregating power and its ability to melt Frank and Evans' icebergs[32] (ordered regions of solvent molecules), one should heed the warning of Emerson and Holtzer[36] concerning the "seductive power" of the concept to explain any experimental result. Thus Schick[28] anticipates from the iceberg picture that a structure-breaking ion should reduce micelle formation, whereas Steigman and Shane[29] use it to argue that a structure-breaking ion should enhance micelle formation. According to Steigman and Shane, the entropy change resulting from micelle formation includes a term corresponding to the destruction of the icebergs around the monomeric surfactant ions when aggregation takes place. If structure-breaking ions are present in solution, the icebergs will "thaw" to a more random state than they would otherwise: hence, a more positive entropy of thawing and a more positive entropy of micellization. Although the explanation can only be qualitative since a number of factors have been disregarded, it is appealing and probably contains a considerable measure of truth.

The arguments of Frank and Evans[32] relative to iceberg rigidity may be invoked to conjure up a more mechanistic explanation of the apparent ability of structure-breaking counterions to promote micellization. Quaternary ammonium ions are structure promoting[31] and the formation of icebergs around dodecyltrimethylammonium and around cetylpyridinium micelles is therefore plausible. If the iceberg is somewhat rigid, counterions which are either structure promoting or only weakly structure breaking may find it difficult to approach the micelle. On the other hand, counterions which are strongly structure breaking would be able to reach the micelle's surface and reduce its charge. This approach receives some support from the p' values of Table II. The large micelles have, on a monomeric basis, effective charges one-half to one-third those of the small micelles. The work of Samis and Hartley,[3] Ford, *et al.*,[16] and Meguro and Kondo[20] demonstrates that ion binding by micelles decreases in the order $I^- > Br^- > Cl^-$, which is in harmony with our mechanistic picture.

Mukerjee and Ray[37] have obtained evidence based on charge-transfer spectra that an interaction over and above that of an electrostatic nature exists between iodide and pyridinium ions. This would in part explain the high aggregating power of the iodide ion.

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(25) E. D. Goddard, C. A. J. Hoeve, and G. C. Benson, *J. Phys. Chem.*, **61**, 593 (1957).
(26) K. W. Herrmann, *ibid.*, **66**, 295 (1962).
(27) G. Nemethy and H. A. Scheraga, *ibid.*, **66**, 1773 (1962).
(28) M. J. Schick, *ibid.*, **68**, 3585 (1964).
(29) J. Steigman and N. Shane, *ibid.*, **69**, 968 (1965).
(30) P. Mukerjee, *Advan. Colloid Interface Sci.*, **1**, 241 (1967).
(31) E. C. Bingham, *J. Phys. Chem.*, **45**, 885 (1941).
(32) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).
(33) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., Inc., New York, N. Y., 1953, Chapters 9, 10.
(34) M. Kaminsky, *Discussions Faraday Soc.*, **24**, 171 (1957).
(35) G. Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 2950 (1929).
(36) M. F. Emerson and A. Holtzer, *J. Phys. Chem.*, **71**, 3320 (1967).
(37) P. Mukerjee and A. Ray, *ibid.*, **70**, 2144 (1966).