



Counterion influence on micelle size  
by Hirendra M Ghose

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree  
of Doctor of Philosophy in Chemistry  
Montana State University  
© Copyright by Hirendra M Ghose (1961)

**Abstract:**

The effect of the counterion upon the size of micelles formed from the dodecyltrimethylammonium and cetylpyridinium ions was studied by light scattering. With respect to the halide ions, the aggregating power increases in the order:  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $CNS^-$  (pseudohalide),  $I^-$ . With respect to the oxyanions, the aggregating power increases in the order:  $IO_3^-$ ,  $CHO_2^-$ ,  $BrO_3^-$ ,  $NO_3^-$ ,  $ClO_3^-$ ,  $ClO_4^-$ . The orders cited are in essential agreement with the lyotropic series of anions.

COUNTERION INFLUENCE ON MICELLE SIZE

by

Hirendra M. Ghose

A THESIS

Submitted to the Graduate Faculty

in

partial fulfillment of the requirements

for the degree of


Doctor of Philosophy in Chemistry


at

Montana State College

Approved:

  
Head, Major Department

  
Chairman, Examining Committee

  
Dean, Graduate Division

Bozeman, Montana  
August, 1961

D 378  
G 346  
cop. 2

TABLE OF CONTENTS

	Page
Abstract . . . . .	3
Introduction . . . . .	4
Light Scattering Equations . . . . .	8
Preparation of Materials . . . . .	11
Scattering Instrument. . . . .	12
Calibration of the Scattering Instrument . . . . .	14
Differential Refractometer . . . . .	22
Calibration of the Differential Refractometer. . . . .	22
Experimental Procedures and Conditions . . . . .	23
Experimental Results . . . . .	25
Discussion . . . . .	40
Summary. . . . .	45
Literature Cited . . . . .	47
Vitae. . . . .	49
Acknowledgments. . . . .	50

151252

ABSTRACT

The effect of the counterion upon the size of micelles formed from the dodecyltrimethylammonium and cetylpyridinium ions was studied by light scattering. With respect to the halide ions, the aggregating power increases in the order:  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $CNS^-$  (pseudohalide),  $I^-$ . With respect to the oxyanions, the aggregating power increases in the order:  $IO_3^-$ ,  $CHO_2^-$ ,  $BrO_3^-$ ,  $NO_3^-$ ,  $ClO_3^-$ ,  $ClO_4^-$ . The orders cited are in essential agreement with the lyotropic series of anions.

## INTRODUCTION

Surface active compounds (surfactants) have been studied extensively for a number of years - on the technical level because of their great importance as cleansing and emulsifying agents and on the academic level because of certain interesting properties of their aqueous solutions.

The conductivity of a surfactant solution is much greater than its osmotic activity would indicate. To explain this anomaly, McBain (22) in 1913 suggested that a considerable quantity of the surfactant exists in solution in colloidal form. Reduction of the number of solute particles in solution through the aggregation of the long-chain ions to form micelles would explain the low osmotic activity that is observed. Because the charged micelles offer less resistance to flow than does an equivalent number of charged single ions, the solution conductivity is relatively high.

Many investigators have attempted to characterize the structure of micelles. According to McBain (22) (23) two different species coexist, a spherical, hydrated, ionic micelle and a relatively large, lamellar, weakly-conducting micelle. In the lamellar micelle the molecules are arranged parallel and adjacent to one another in double layers, each layer being twice the length of a molecule.

Hartley (16) took the view that all properties of surfactant solutions could be explained on the basis of one kind of aggregate - the spherical micelle. Such an aggregate would have a chaotic paraffin interior of radius equal to the length of a fully extended chain. The actual radius of the micelle would be somewhat larger than this because of

the volume requirements of the polar heads, attached gegenions and the hydration layer. Hartley and Runnicles (17) measured the diffusion coefficients of cetylpyridinium chloride in the presence of various supporting electrolytes. Micelle radii calculated from the Stokes-Einstein equation were all in the neighborhood of  $26\text{\AA}$ , a value which was deemed to be reasonable for a spherical micelle of a surfactant with 16 carbons in the chain. The calculated radii were independent, within experimental error, of the concentration of surfactant and supporting electrolyte. Hartley and Runnicles cited these results as being in "excellent agreement with the 'spherical liquid' micelle' theory."

Vetter (37) accepted the spherical micelle of Hartley, but suggested that the solvent penetrates its interior. The solvent concentration within the micelle decreases with the depth of penetration, leaving the core of the micelle a pure hydrocarbon.

Harkins and his co-workers (15) concluded from the results of their X-ray work that surfactant micelles are cylindrical, the paraffin chains forming the bodies of the cylinders and the polar groups the ends. Corrin (8) later concluded that the X-ray patterns did not permit one to differentiate between cylindrical and spherical micelles.

Tartar (35), after reviewing the results of a number of investigations concerned with the determination of micellar weights, concluded that the micelle may have either spherical or oblate spheroidal shape. He pointed out that the apparent constancy of micelle radii found by Hartley and Runnicles for cetylpyridinium chloride did not necessarily rule out non-spherical micelles for this surfactant. The Stokes-Einstein equation is

only valid for spherical particles.

In the presence of sufficient supporting electrolyte, the micelles of some surfactants are definitely nonspherical. Debye and Anacker (11) concluded from dissymmetry measurements with cetyltrimethylammonium bromide in the presence of added KBr that the micelles of this surfactant are rod-like in shape. The flow birefringence experiments of Scheraga and Backus (28), the light scattering work of Trap and Hermans (36), and the conductivity measurements of Götz and Heckman (13) support this view.

Another example of nonspherical micelles can be given. Scott et al. (30) computed that spherical micelles of octyltrimethylammonium octanesulfonate ( $C_8-C_8$ ) would contain about 13 cations and 13 anions. This corresponds to a micellar weight of less than 5,000. Anacker (2) investigated this surfactant by light scattering and found a micellar weight of 21,600. Since this was more than four times larger than the value given by Scott, Anacker concluded that the  $C_8-C_8$  micelles could not be Hartley spheres.

Factors affecting micelle size such as chain length and concentration of added simple electrolyte have been studied extensively (1) (29) (34) (35). Relatively little attention, however, has been paid to the role played by the counterion. The diffusion experiments of Hartley and Rummicles previously cited revealed "a definite though small influence of the nature of the gegenions." In a brief study of the effect of the gegenion on tetradecyltrimethylammonium bromide micellar weights, Anacker (1) observed that the bromide, chloride and nitrate ions had different influences, whereas ions with charges of the same sign as that of the micelle had little or no effect. Princen and Mysels (26) examined solutions of sodium, lithium, and

tetramethylammonium laurylsulfate by light scattering. Substitution of lithium for sodium increased the aggregation number from 62 to 63. Substitution of the tetramethylammonium ion for sodium resulted in an appreciable increase in the aggregation number -62 to 76.

From his investigations of the conductivities of solutions of various octadecyltrimethylammonium salts in water, Grieger (14) concluded that the critical micelle concentration and the slope of the equivalent conductance vs. concentration plot show marked dependence on the gegenion.

The present investigation was undertaken to augment the rather limited information available concerning the role played by the counterion in influencing the properties of micelles and their solutions.

Originally it was planned to examine the micelles formed by dodecyltrimethylammonium bromide, -chloride, -fluoride, -nitrate, -chlorate, etc., and the micelles formed by cetylpyridinium bromide, -chloride, -fluoride, -nitrate, -chlorate, etc. Because of the enormity of the task of preparing relatively large and pure samples of so many surfactants, the original plan was abandoned in preference for the following one. Pure samples of dodecyltrimethylammonium bromide (DTAB) and cetylpyridinium bromide (CPB) would be prepared. Solutions of these surfactants in the presence of relatively large amounts of the salts NaF, NaCl, NaBr, NaNO<sub>3</sub>, NaBrO<sub>3</sub>, NaIO<sub>3</sub>, NaCHO<sub>2</sub> and NaSCN would be studied.

The light scattering technique was chosen for this investigation because of its proven success and wide range of applicability.



LIGHT SCATTERING EQUATIONS

The data collected in this investigation were treated in accordance with the equation

$$(1) \quad H \frac{C - C_0}{T - T_0} = \frac{q}{M_m} \left[ 1 + \frac{C - C_0}{2M_m} \frac{p^2 + p - pq}{n_1 + n_3} + o(C - C_0)^2 + \dots \right]$$

which is based upon the general fluctuation theory of light scattering by multicomponent systems; it was developed for surfactant solutions by Prins and Hermans (27) and Princen and Mysels (26). The equation is subject to the assumption of monodispersity and constancy of activity coefficient, charge, aggregation number, and monomer concentration above the critical micelle concentration,  $C_0$ . The critical micelle concentration marks a small concentration range in which abrupt changes of solution properties take place and micelles begin to form in large numbers. If the system is polydisperse, if the size distribution is independent of concentration, and if the ratio of the micelle charge to the aggregation number is the same for all species, the measured micellar molecular weight and charge are simple weight averages. In equation (1),  $C$  is the total concentration of the surfactant in g/ml and  $M$  is the micellar weight.  $T$  is the turbidity\* of the solution of concentration  $C$  and  $T_0$  is the turbidity of the solution at the critical micelle concentration.

$H$  is given by

---

\*In the case of conservative absorption, the turbidity of a medium is defined by  $(1/L) \ln I_0/I$ , where  $I_0$  and  $I$  are respectively the intensity of the incident and exiting light and  $L$  is the path length through the scattering medium.

$$(2) \quad \frac{H}{H_0} = \frac{32\pi^3 n_0^2 \left( \frac{n - n_0}{C} \right)^2}{3N\lambda^4}$$

where  $n$  and  $n_0$  are respectively the refractive index of the solution and the refractive index of the solvent.  $N$  is Avogadro's number,  $C$  is the solute concentration in grams per milliliter, and  $\lambda$  is the wavelength of the incident light.

In equation (1)  $p$  is the micellar charge,  $n_1$  and  $n_3$  are respectively the critical concentration and supporting electrolyte concentration in moles/ml., and  $T - T_0$  represents the difference in turbidity between a solution of concentration  $C$  and of concentration  $C_0$ . Here  $q$  is given by

$$q = (n_1 + n_3)^2 / (n_1^2 d_1 + 2n_1 n_3 d_2 + n_3^2 d_3)$$

in which

$$d_1 = 1 - p/m + p^2/4m^2 + p/4m^2$$

$$d_2 = 1 - p/2m - fp/2m + fp^2/4m^2 + fp/4m^2$$

$$d_3 = 1 - fp/m + f^2 p^2/4m^2 + f^2 p/4m^2$$

The aggregation number  $m$  is the number of surfactant ions per micelle. The ratio of the molar refractive index increment of the added salt to that of the surfactant is designated by  $f$ . The supporting electrolyte has one ion in common with the surfactant. All ions except the micelle are univalent.

If  $p$  and  $m$  may be treated as constants, equation (1) implies that for a given simple salt concentration a plot of  $H(c - C_0)/(T - T_0)$  vs.  $C - C_0$  should yield at concentrations near the  $C_0$  a straight line with intercept

$$(3) \quad A = q/mM_1$$

and slope

$$(4) \quad B = A(p^2 + p - AmM_1p)/(2mM_1)(n_1 + n_3)$$

Elimination of m between (3) and (4) gives

$$(5) \quad p = \frac{2EM_1(n_1 + n_3)(n_1 + fn_3) \pm 2(n_1 + n_3)(2Bn_1 + 2Bn_3)^{\frac{1}{2}}}{2A(n_1 + n_3) - A^2M_1(n_1 + fn_3)}$$

Once p is found from (5), m may be computed from

$$(6) \quad m = \frac{1}{2}(pE + 1/AM_1) \pm \frac{1}{2} \left[ (pE + 1/AM_1)^2 - (p^2 + p)E^2 \right]^{\frac{1}{2}}$$

where E is given by

$$(7) \quad E = (n_1 + fn_3)/(n_1 + n_3)$$

Taken at face value, a horizontal plot ( $B = 0$ ) of  $H \frac{C - C_0}{T - T_0}$  vs.

$C - C_0$  implies that the micellar charge is zero. The micellar charge has, in all likelihood, not been reduced to zero, but the theory instead has become inadequate and no charge correction to the micellar weight is possible. With B set equal to zero, equation (1) becomes

$$(8) \quad H \left[ \frac{C - C_0}{T - T_0} \right]_{C - C_0 = 0} = 1/M_m$$

According to calculations made by Anacker and Westwell (3) neglect of the charge correction in the dodecylammonium chloride results in micellar weights which are about 10% too small in water and less than 2% low in 0.05 molar NaCl. This would indicate that equation (8) is applicable to the present work since supporting electrolyte concentrations of

0.1 molar or greater were used in all experiments.

#### PREPARATION OF MATERIALS

Dodecyltrimethylammonium bromide was prepared by refluxing dodecylbromide with a 25% alcoholic solution of trimethylamine according to the method of Scott and Tartar (29). The crude compound was crystallized several times from acetone with a small percentage of ethanol present. In the final recrystallization, ether was added to an acetone-alcohol solution of the surfactant until precipitation started. Dodecylbromide and trimethylamine in 25% methanol were from the Eastman Kodak Company. The bromide content was determined gravimetrically: 25.92% Br found; 25.92% Br theoretical.

Cetylpyridinium bromide was prepared by refluxing 1-bromo hexadecane and pyridine at 120° - 130° C. for four hours. The pyridine and 1-bromo hexadecane were of reagent grade. The crude CPB was purified by repeated recrystallization from water, benzene, pyridine, water-acetone and ethanol-water. The bromide content of CPB was determined gravimetrically: 20.78% found; 20.79% theoretical.

Dodecyltrimethylammonium chloride was prepared from dodecyltrimethylammonium bromide by repeated crystallization from a saturated sodium chloride solution. The product was then recrystallized several times from water, acetone, alcohol, and finally from a mixture of acetone and ether. The chloride content was determined gravimetrically: 13.44% Cl found; 13.43% Cl theoretical. In the case of all three surfactants, water and solvent were removed by vacuum desiccation and storage over  $P_4O_{10}$ .

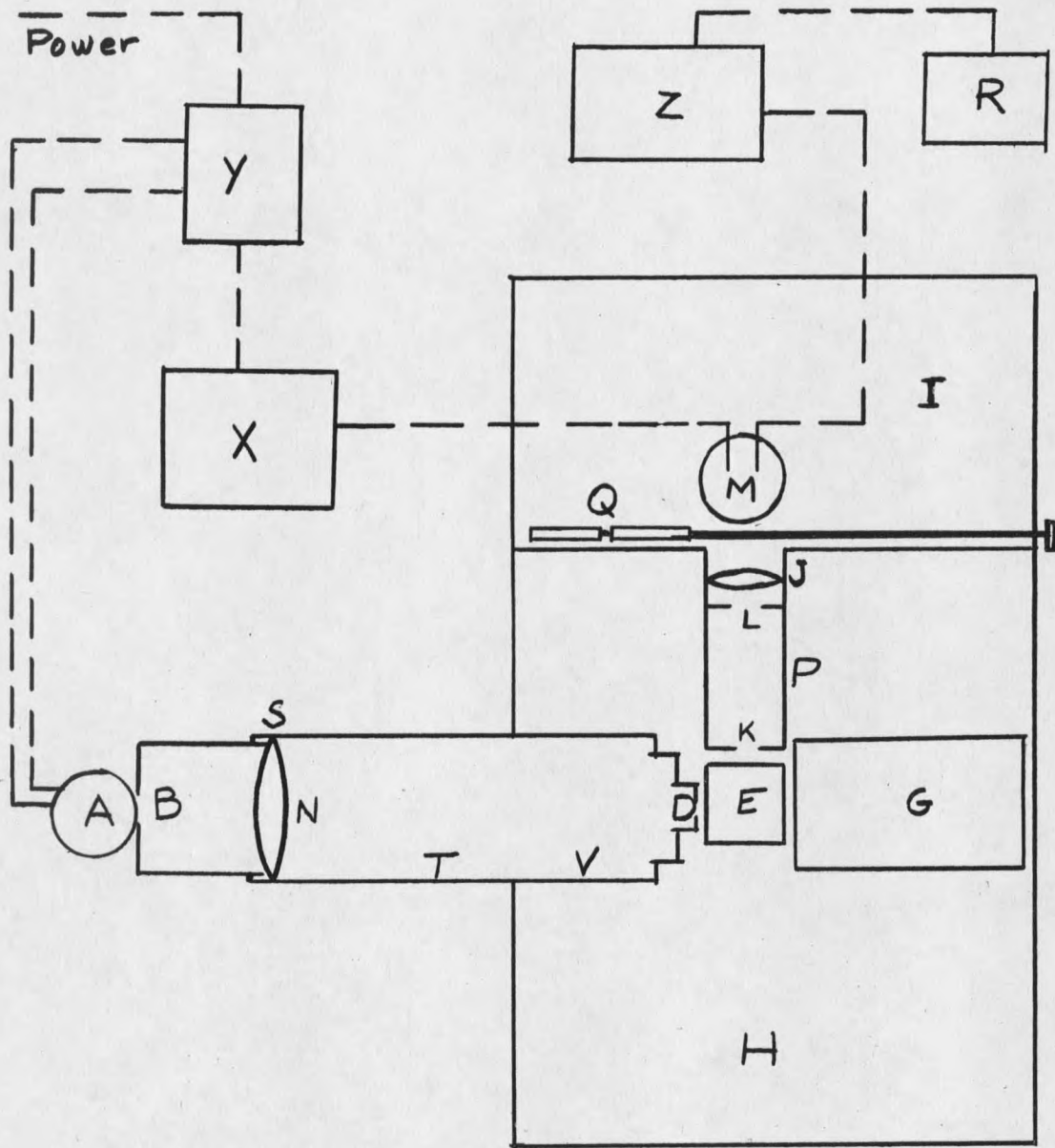
Reagent grade silicotungstic acid (Allied Dye Chemical Corporation) was crystallized six times from water. After vacuum desiccation and storage over  $\text{CaCl}_2$  for several days, the acid was analyzed for water by the method of Kolthoff and Sandell (19). Its composition may be represented as  $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$ .

#### SCATTERING INSTRUMENT

Molecular weight determinations by light scattering require a comparison of the intensities of incident and scattered light. A number of instruments which accomplish this comparison have been reported in the literature (4)(6)(9)(10)(20)(31). The apparatus shown in figure 1 was designed and built for the present investigation. The incident light is supplied by high pressure mercury arc A (G.E. 100 watt AH-4). Fluctuations in intensity are kept to a low level through the use of Voltage Stabilizer Y (Raytheon Manufacturing Company, 250 watts) and a ballast lamp in the circuit. The lamp base is provided with screws which may be used to lock the lamp in position after focusing of the beam has been completed.

Aperture B is circular and  $3/16$ " in diameter. It is located one focal length (4.5 cm.) from lens N. Exit slit D is rectangular in cross section ( $3/16$ " x  $7/16$ "). Since B, lens support S, V, and the inside of T are threaded, various components of the instrument's collimating system can be adjusted easily and reproducibly. The design of the collimating system also permits rapid exchange of slits, apertures, and lenses.

The light scattering compartment H contains a scattering cell; two adjustable tubes, V through which incident light enters and P through



A SCHEMATIC DIAGRAM OF  
90° SCATTERING INSTRUMENT

Fig. 1.

which the  $90^\circ$  scattered light exits; and a light trap G. The scattered light is collimated by means of two circular apertures, K and L, of  $3/16$ " diameter placed between the scattering cell E and the lens J, which focuses the light on the phototube. The photomultiplier housing I is light tight and electrically shielded; it contains an RCA IP21 photomultiplier tube M, a voltage divided resistance network, and a shutter-filter combination Q. Mounted on the shutter are two Baird interference filters - one for isolating the  $4358\text{\AA}$  line (blue), and one for isolating the  $5451\text{\AA}$  line (green).

The output of the photomultiplier tube is fed to a Beckman micro-microammeter Z, Model RXG2, and then recorded on 10 mv. Minneapolis Honeywell recorder, R.

#### CALIBRATION OF THE SCATTERING INSTRUMENT

An important step in the determination of molecular weights by light scattering is the calibration of the scattering instrument. As will be shown, success of the method depends upon the accurate determination of the ratio of the intensity of the light scattered at an angle, usually  $90^\circ$ , to that of the incident light. Since this ratio is of the order of  $10^{-6}$ , it is not easy to compare the intensities directly. In practice one either uses neutral filters in front of the photomultiplier tube when monitoring the incident light to cut its intensity to a value close to that of the scattered light or one compares the light scattered at  $90^\circ$  from solutions with that scattered at the same angle from a standard. We have used the latter method with a polished lucite block serving as a standard. The theory is outlined on the following pages.

If  $i_{\theta}$  is the intensity of light scattered by a unit volume of solution in excess of that scattered by the solvent at a distance  $r$  and at an angle  $\theta$  to the incident light, which is unpolarized and has an intensity of  $I_0$ , the turbidity of the solution in excess of the solvent is given by

$$(9) \quad T = \int_0^{\pi} \frac{i_{\theta} 2\pi r^2 \sin \theta d\theta}{I_0}$$

If the solute particles are small, isotropic, and are dielectrics,  $i_{\theta}$  in dilute solutions is given by

$$i_{\theta} = i_{90} (1 + \cos^2 \theta)$$

If this is substituted into equation (9) and the integration performed, the following expression for the turbidity is obtained.

$$(10) \quad T = \frac{16\pi}{3} R_{90}$$

in which  $R_{90} = r^2 i_{90}/I_0$ . Thus, one sees that the turbidity -- and, consequently, the molecular weight of the solute -- depends upon the determination of the ratio of the intensities of the scattered light and the incident light, i.e., upon  $i_{90}/I_0$ .

In practice, one measures a quantity  $G_{90}$  which represents the difference

$$\frac{g(\text{solution})}{g(\text{standard})} - \frac{g(\text{solvent})}{g(\text{standard})}$$

The  $g$ 's are instrument readings and are proportional to the intensities of the light scattered at  $90^\circ$ .  $G_{90}$  and  $R_{90}$  are related by

$$(11) \quad R_{90} = k C_v C_n G_{90}$$




The factors  $C_v$  and  $C_n$  are required to convert a measured  $G_{90}$  into one which would have been obtained if the volume "seen" by the photomultiplier tube had been the same as that defined by the apertures between the scattering cell and the detector and if the scattered light rays, on leaving the cell, had not spread. Since  $C_v$  and  $C_n$  are functions of the refractive index, they will change whenever the solvent and the wavelength are changed. Therefore, they cannot be incorporated into the instrument constant  $k$ .


Carr and Zimm (6) were the first investigators to stress the need for making the corrections implied by  $C_v$  and  $C_n$ . The procedures followed in this work to compute these correction factors will be outlined briefly.

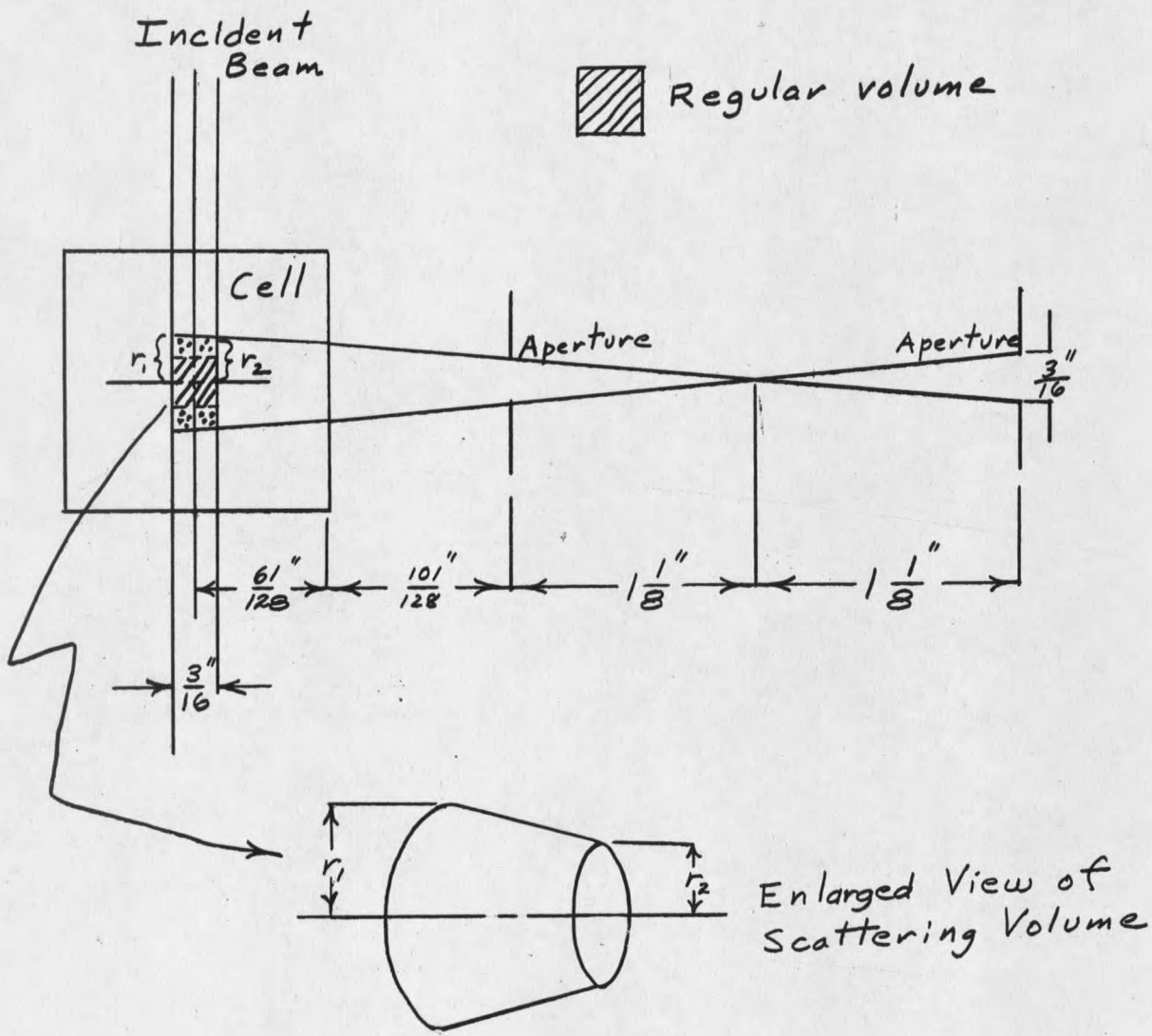
Consider first the volume correction  $C_v$ . Figure 2 is pertinent to our discussion. It is clear from the experimental arrangement that the photomultiplier tube registers some light scattered from volume elements outside the "regular" volume (crosshatched in figure) defined by the detector apertures. The "excess" volume (stippled in figure) varies with the solvent used.  $C_v$  is defined by

$$C_v = \frac{\text{regular volume}}{\text{regular volume} + \frac{\text{excess volume}}{2}}$$

The assumption made in this relationship is that volume elements in the excess volume are on the average only 1/2 as effective as those in the regular volume as far as sending light to the photomultiplier tube is concerned. The elements in the regular volume form approximately the same solid angle with respect to the photomultiplier tube, but elements in the excess volume form smaller scattering solid angles which decrease from a maximum at the regular volume -- excess volume boundary to zero at the

 Excess volume

 Regular volume



VOLUME CORRECTION  $C_V$

FIG. 2

outer boundary.

In terms of the dimensions given in figure 2 for the scattering volume

$$C_v = \frac{1}{0.5000 + 18.96 (r_1^2 + r_1 r_2 + r_2^2)}$$

The radii  $r_1$  and  $r_2$  depend upon the refractive index of the scattering solution and instrumental geometry. In the notation of figure 3,  $r_1$  and  $r_2$  are given by

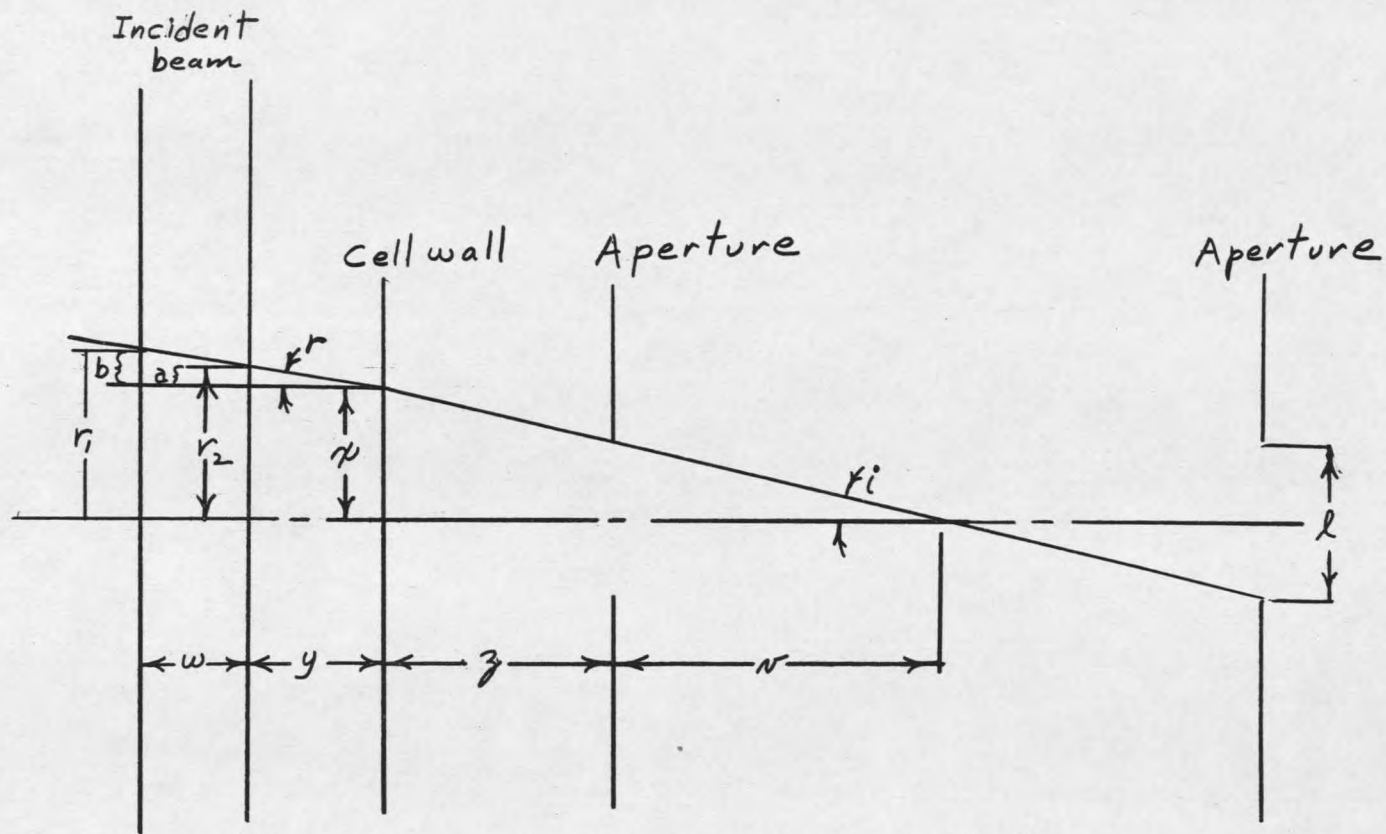
$$r_1 = \frac{(z + v)l}{2v} + (y + w)l / \left[ l^2(n^2 - 1) + 4v^2n^2 \right]^{1/2}$$

$$r_2 = \frac{(z + v)l}{2v} + yl / \left[ l^2(n^2 - 1) - 4v^2n^2 \right]^{1/2}$$

The values of  $w$ ,  $y$ ,  $z$ ,  $v$ , and  $l$  for the instrument used in this investigation are respectively  $3/16$ ,  $49/128$ ,  $101/128$ ,  $9/8$  and  $3/16$ ".

The refractive index correction  $C_n$  depends both on the shape of the scattering cell and the refractive index of the scattering medium. Figure 4 illustrates this. It represents a top view of the scattering cell and the apertures in front of the photomultiplier tube. For purposes of clarity, it was not drawn to scale. The flux originating from a particle at  $O$  and collected by the photometer is in the angle  $\theta_1$ . If there were no refraction at the cell wall, the photometer would collect the flux contained in the angle  $\theta_2$ . Correction factors for spherical, cylindrical, and rectangular cells are respectively 1,  $\theta_2/\theta_1$ , and  $(\theta_2/\theta_1)^2$ . Carr and Zimm (6) find for the rectangular cell, which was used in the present work,

$$C_n = (\theta_2/\theta_1)^2 = n^2 \left[ 1 - \frac{a(n-1)}{bn} \right]^2 . \text{ In our instrument } a = 61/128 \text{ and}$$



CALCULATION OF  $r_1$  AND  $r_2$

Fig. 3.









































































