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COUNTERION INFLUENCE ON MICELLE SIZE

by

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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 26Å, 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 nonspherical 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 Runnicles 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 cetylpridinium bromide (CPB) would be prepared. Solutions of these surfactants in the presence of relatively large amounts of the salts NaF, NaCl, NaBr, $NaNO_3$, $NaBrO_3$, $NaIO_3$, $NaCHO_2$, 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

$$(1) \quad H \frac{C - C_o}{T - T_o} = \frac{q}{M_m} \left[1 + \frac{C - C_o}{2M_m} \frac{p^2 + p - pq}{n_1 + n_3} + O(C - C_o)^2 + \ldots \right]$$

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_o. 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_o is the turbidity of the solution at the critical micelle concentration.

H is given by

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

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

where n and n_o 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 λ 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 $T - T_o$ represents the difference in turbidity between a solution of concentration C and of concentration C_o. 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

$$d_1 = 1 - p/m + p^2/4m^2 + p/4m^2$$
$$d_2 = 1 - p/2m - fp/2m + fp^2/4m^2 + fp/4m^2$$
$$d_3 = 1 - fp/m + f^2p^2/4m^2 + f^2p/4m^2$$

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 $H(c - C_o)/(T - T_o)$ vs. $C - C_o$ should yield at concentrations near the C_o a straight line with intercept

(3) $A = q/mM_1$

and slope

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

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

(5) $$p = \frac{2BM_1(n_1 + n_3)(n_1 + fn_3) \pm 2(n_1 + n_3)(2Bn_1 + 2Bn_3)^{\frac{1}{2}}}{2A(n_1 + n_3) - A^2M_1(n_1 + fn_3)}$$

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

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

where E is given by

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

Taken at face value, a horizontal plot $(B = 0)$ of $H\frac{C - C_o}{T - T_o}$ vs. $C - C_o$ 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) $$H\left[\frac{C - C_o}{T - T_o}\right]_{C - C_o = 0} = 1/M_m$$

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 that 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}.

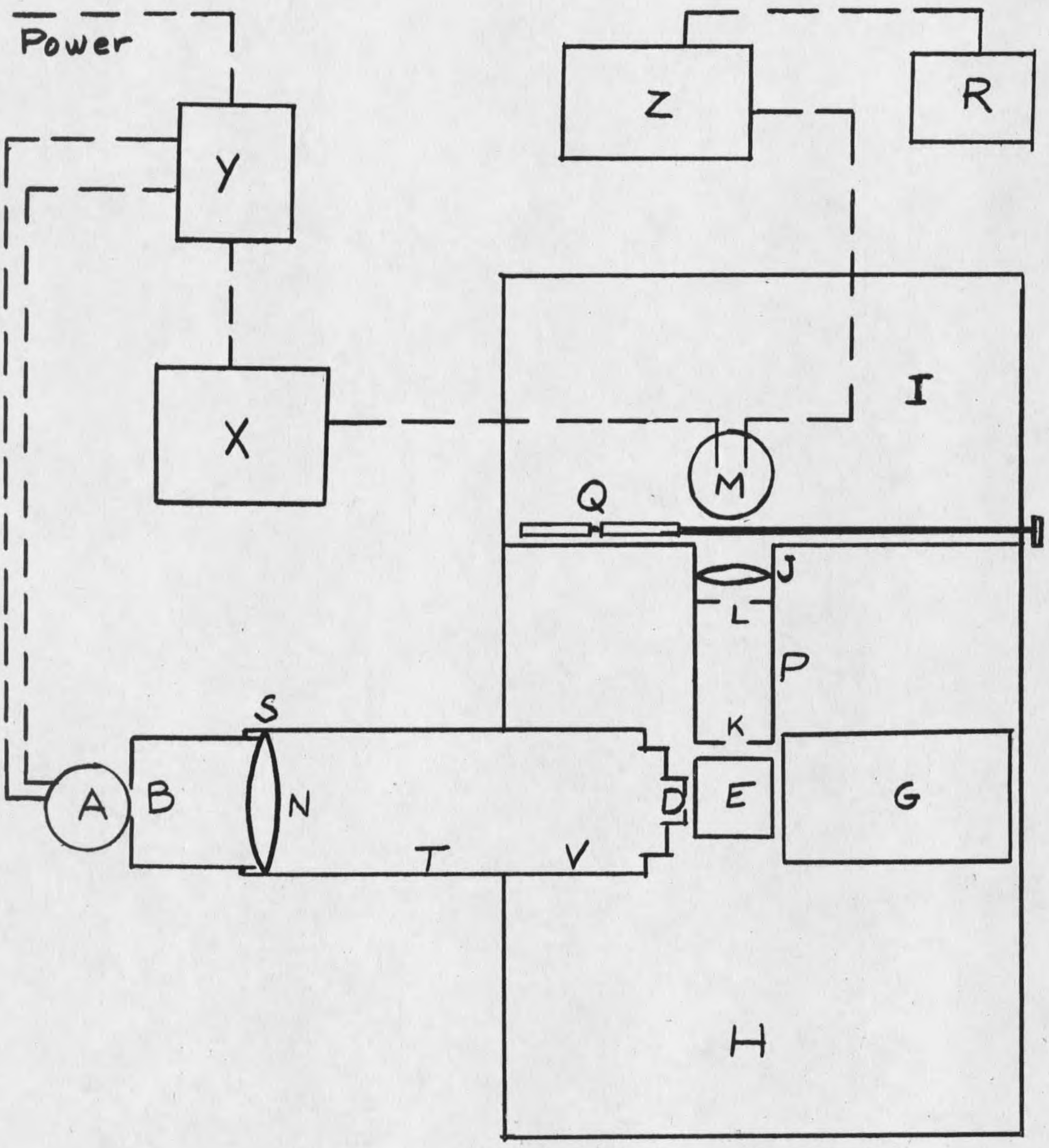
Reagent grade silicotungstic acid (Allied Dye Chemical Corporation) was crystallized six times from water. After vacuum desiccation and storage over $CaCl_2$ for several days, the acid was analyzed for water by the method of Kolthoff and Sandell (19). Its composition may be represented as $H_4SiW_{12}O_{40}$, $14H_2O$.

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° 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 4358Å line (blue), and one for isolating the 5451Å 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°, 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° 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_Θ 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 Θ to the incident light, which is unpolarized and has an intensity of I_o, the turbidity of the solution in excess of the solvent is given by

$$T = \int_0^{\pi} \frac{i_\Theta \, 2\pi r^2 \sin \Theta \, d\Theta}{I_o} \tag{9}$$

If the solute particles are small, isotropic, and are dielectrics, i_Θ 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.

$$T = \frac{16\pi}{3} \, R_{90} \tag{10}$$

in which $R_{90} = r^2 \, i_{90}/I_o$. Thus, one see 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_o.

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°. G_{90} and R_{90} are related by

$$R_{90} = kC_v C_n G_{90} \tag{11}$$

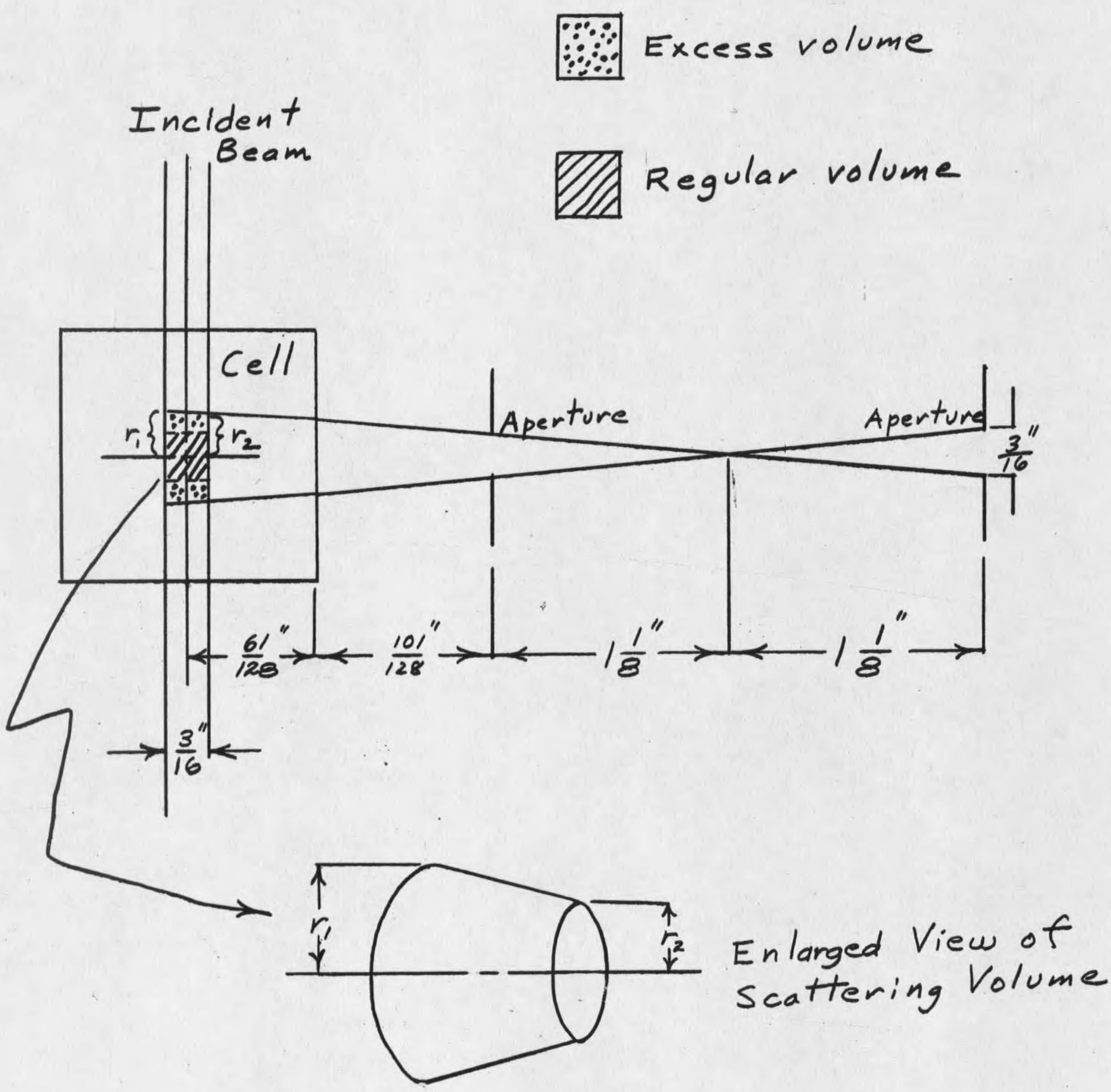
The factors C_v and C_n are required to convert a measured G_{90} into one which would have been obtained if the volume "seen" by the photomultiplier tube had been the same as that defined by the apertures between the scattering cell and the detector and if the scattered light rays, on leaving the cell, 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 aperatures. 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



VOLUME CORRECTION C_V

FIG. 2

outer boundary.

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

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

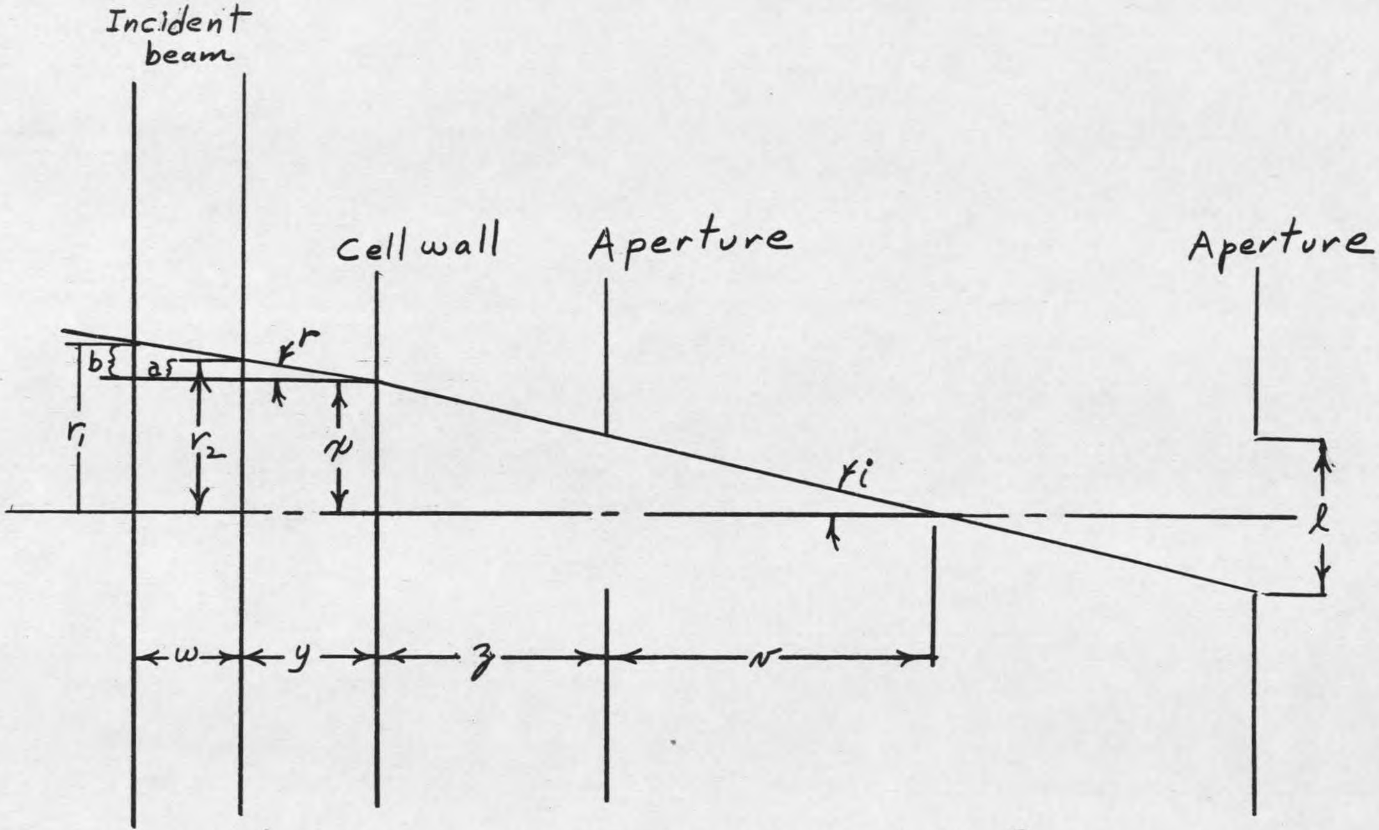
The radii r_1 and r_2 depend upon the refractive index of the scattering solution and instrumental geometry. In the notation of figure 3, r_1 and r_2 are given by

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

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

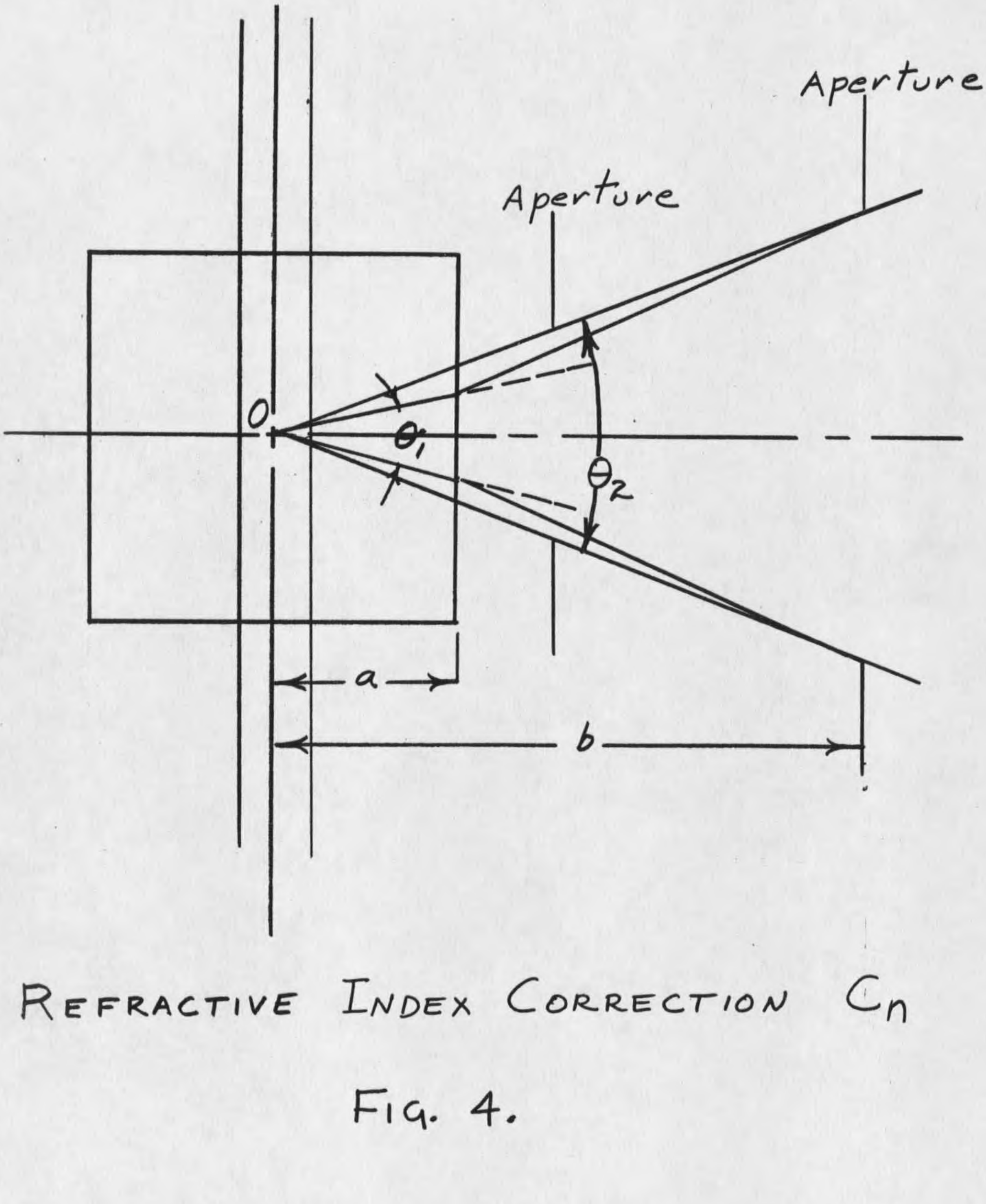
The values of w, y, z, v, and l for the instrument used in this investigation are respectively 3/16, 49/128, 101/128, 9/8 and 3/16".

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 0 and collected by the photometer is in the angle θ_1. If there were no refraction at the cell wall, the photometer would collect the flux contained in the angle θ_2. Correction factors for spherical, cylindrical, and rectangular cells are respectively 1, θ_2/θ_1, and $(\theta_2/\theta_1)^2$. Carr and Zimm (6) find for the rectangular cell, which was used in the present work, $C_n = (\theta_2/\theta_1)^2 = n^2\left[1 - \frac{a(n-1)}{bn}\right]^2$. In our instrument a = 61/128 and



CALCULATION OF r_1 AND r_2

Fig. 3.



REFRACTIVE INDEX CORRECTION C_n

FIG. 4.

$b = 3\frac{33}{64}''$.

Computed values of C_v and C_n for various solvents may be found in Table I.

The instrument constant k was determined through a comparison of the scattering of several solutions of known turbidity with that of the lucite block and substitution of the experimental data into the expression

$$k = 3T/16\pi C_v C_n G_{90}$$

Employed as standards were a 0.7304 molar solution of sucrose in water, a 1/2% solution of polystyrene (obtained from Cornell University) in toluene, and a 0.03706 molar solution of silicotungstic acid in water. The turbidities of these solutions as reported in the literature (18)(21) (or as computed from data in the literature (33)) and the corresponding k's determined with their use are given in Table I. Each k in the table represents the average of at least two separate runs. The precision obtained is discernible from a comparison of the separate results with the silicotungstic acid. For blue light values of $k \times 10^4$ found were 1.77, 1.78, 1.76, and 1.80. For green light values found were 1.66, 1.68, 1.67, 1.71. Differences between the various averages in the table represent experimental errors not only in the present investigation but also in the original turbidity determinations. In view of the number of different instruments and investigators involved and of the relative primitiveness of the light scattering art, it is felt that the agreement among the average k values in the table is about as good as one could expect. In the evaluation of the light scattering data (only blue light used) obtained with the

TABLE I

CALIBRATION OF 90° SCATTERING INSTRUMENT

Blue Light (4358Å)

Scattering Medium	C_n	C_v	C_{90}	T	k
½% polystyrene in toluene	2.089	0.4063	1.411	3.50×10^{-3}	1.74×10^{-4}
Water	1.6735	0.3945			
0.7304 molar sucrose	1.7558	0.3972	0.2082	3.48×10^{-4} 3.47×10^{-4}	1.69×10^{-4}
0.03706 molar silicotungstic acid	1.7011	0.3953	0.1514	2.42×10^{-4}	1.78×10^{-4}

Green Light (5461Å)

Scattering Medium	C_n	C_v	C_{90}	T	k
½% polystyrene in toluene	2.036	0.405	0.576	1.35×10^{-3}	1.70×10^{-4}
Water	1.6606	0.3940			
0.7304 molar sucrose	1.7411	0.3968	0.0996	1.41×10^{-4} 1.36×10^{-4}	1.66×10^{-4} 1.60×10^{-4}
0.03706 molar silicotungstic acid	1.6865	0.3948	0.0725	0.85×10^{-4}	1.68×10^{-4}

surfactants studied in this work, a k value of 1.74×10^{-4} was used.

DIFFERENTIAL REFRACTOMETER

Since the concentration gradient of the refractive index, dn/dc, occurs as a squared term in the light scattering equation, its accurate determination is of considerable importance.

For the range of concentration used in light scattering, the refractive index difference between solution and solvent will be in the third decimal place. If it is to be determined to an accuracy of 1%, measurements accurate to about 5×10^{-6} are necessary. This is best accomplished in an instrument which measures the difference directly.

The differential refractometer used in this laboratory is similar to the one described by P. P. Debye (12). The deflection of a light beam passing through a partitioned cell containing both solvent and solution is proportional to the difference in the refractive indexes.

Although the temperature coefficient of the gradient is usually small, it is necessary to keep thermal differences between solvent and solution to a minimum. This was accomplished in the present work by mounting the cell in a brass block open only at the top and on the two sides perpendicular to the light beam and by passing water continuously from a thermostat through five holes in the block. The block and cell were housed in a metal chamber inside the instrument.

CALIBRATION OF THE DIFFERENTIAL REFRACTOMETER

The deflections of the light beam produced by four solutions of sodium chloride in water were measured. Their refractive indexes were computed from Stamm's (32) tabulation for sodium chloride solutions. The instrument constant was then taken as the average of the computed ratios of Δn and ΔR, where Δn is the difference in refractive index between solution and solvent and ΔR is the corresponding instrument deflection as observed with the filar micrometer eyepiece. Results of the calibration are listed in Table II.

TABLE II

CALIBRATION OF DIFFERENTIAL REFRACTOMETER

NaCl Molarity	$\Delta n \times 10^3$	ΔR	$\Delta n/\Delta R \times 10^5$
0.06829	0.7280	8.05	9.04
0.11000	1.1679	12.92	9.04
0.14349	1.5197	16.74	9.08
0.19290	2.0362	22.76	9.02
		Average	9.04×10^{-5}

EXPERIMENTAL PROCEDURES AND CONDITIONS

In the light scattering portion of the investigation, solutions were filtered directly into the scattering cell under nitrogen pressure through an ultrafine, fritted Pyrex glass funnel. After its turbidity had been measured, a solution was removed from the cell through a glass capillary with suction provided by a water aspirator.

The uncertainties of an intensity measurement attendant the use of a galvanometer whose needle or spot light is fluctuating (possibly because of Brownian motion and/or thermal moise) were reduced somewhat in this work by registering the amplifier output on a chart recorder. Scattered light intensities were taken as proportional to mean pen positions.

Readings with the lucite standard in the photometer were sandwiched between those with solutions in the instrument so that corrections could be made to compensate for the slow decay of the intensity of the incident light source with time.

In the measurement of the Δn of a solution, the divided cell of the differential refractometer was first filled with solvent and ten readings of the position of the slit image as seen at the eyepiece were taken. The solvent was then replaced on one side of the cell by the solution (five rinses with solution) and ten readings of the position of the displaced slit image were taken. The refractive index difference between solution and solvent was then calculated from the product of the instrument constant and ΔR, the difference in the averages of the two sets of readings, i.e., $\Delta n = 9.04 \times 10^{-5} \Delta R$.

Light of wavelength 4358Å, as isolated by a Baird interference filter, was used in both the scattering and refractive index measurements.

Except for one run at 25° C., DTAB solution turbidities were measured at 31 ± 1° C. CPB turbidities were measured at 33 ± 1° C. Precipitation occurred in certain of the CPB solutions when the temperature was allowed to fall below 32° C. Refractive index measurements were made at 32 ± 0.1° C.

All glassware was cleaned with detergent and chromic acid cleaning solution and rinsed copiously with tap water and with water from a demineralizing column. Water was passed through the fritted glass funnel used in the filtration of all solutions examined in the photometer until the filtrate was neutral to litmus. This often took several hours, indicating that the H^+ from the chromic acid solution is tenaciously held on glass.

EXPERIMENTAL RESULTS

Figures 5 through 12 present the scattering data collected in this investigation as G_{90} vs. surfactant concentration plots. Because of the lack of space, some of the experimental points below the critical micelle concentrations (in the region of the short horizontal lines) have been omitted.

For the ideal situation in which no micelles form until the critical concentration is reached, in which the monomer concentration remains constant thereafter, and in which the micelles are monodisperse and do not change in size with surfactant concentration, the G_{90} plots will break sharply upward at the critical micelle concentration. As the surfactant concentration is increased, the slope gradually decreases. The reciprocal of the initial slope at zero micelle concentration or its equivalent, the intercept of the $(C - C_o)/(G_{90,C}) - (G_{90,C_o})$ vs. $C - C_o$ plot, is designated as I and is related to the micellar weight -- assuming zero charge -- by

$$M = 16\pi k C_v C_n / 3HI.$$

As can be seen in figures 5 through 12 a number of the systems are far from ideal and exhibit marked curvature in the critical micelle region. In these cases, I values were taken as the reciprocals of the slopes of the plots at intermediate concentrations. Micellar weights computed in this manner will possess more uncertainty that if rounding had not occurred at the critical micelle concentrations.

Micellar weights computed from the above expression are given in

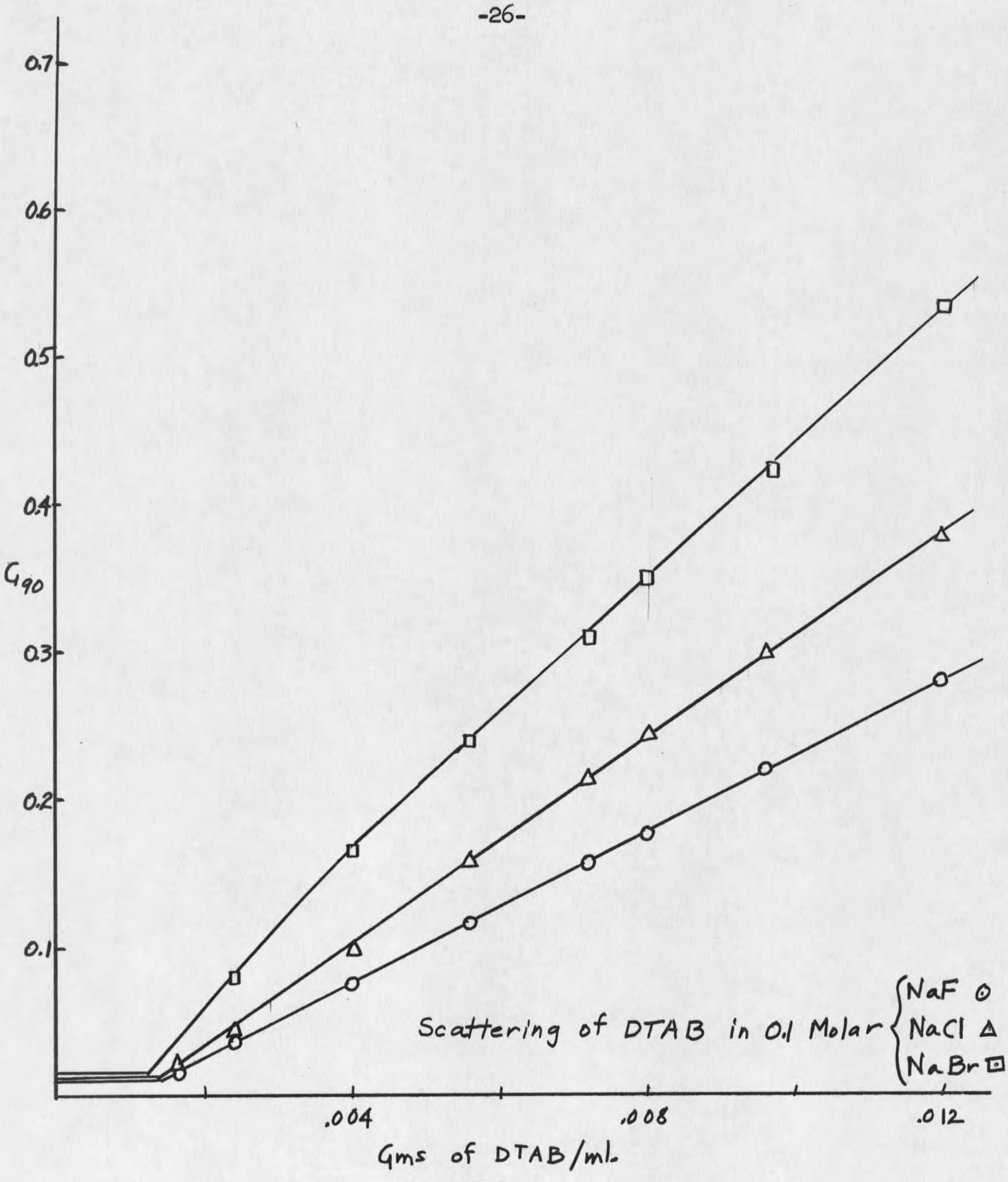

0.7
0.6
0.5
0.4
0.3
0.2
0.1
G_{90}
.004
.008
.012
Gms of DTAB/ml.
Scattering of DTAB in 0.1 Molar
NaF ○
NaCl △
NaBr ⊡

Fig. 5.

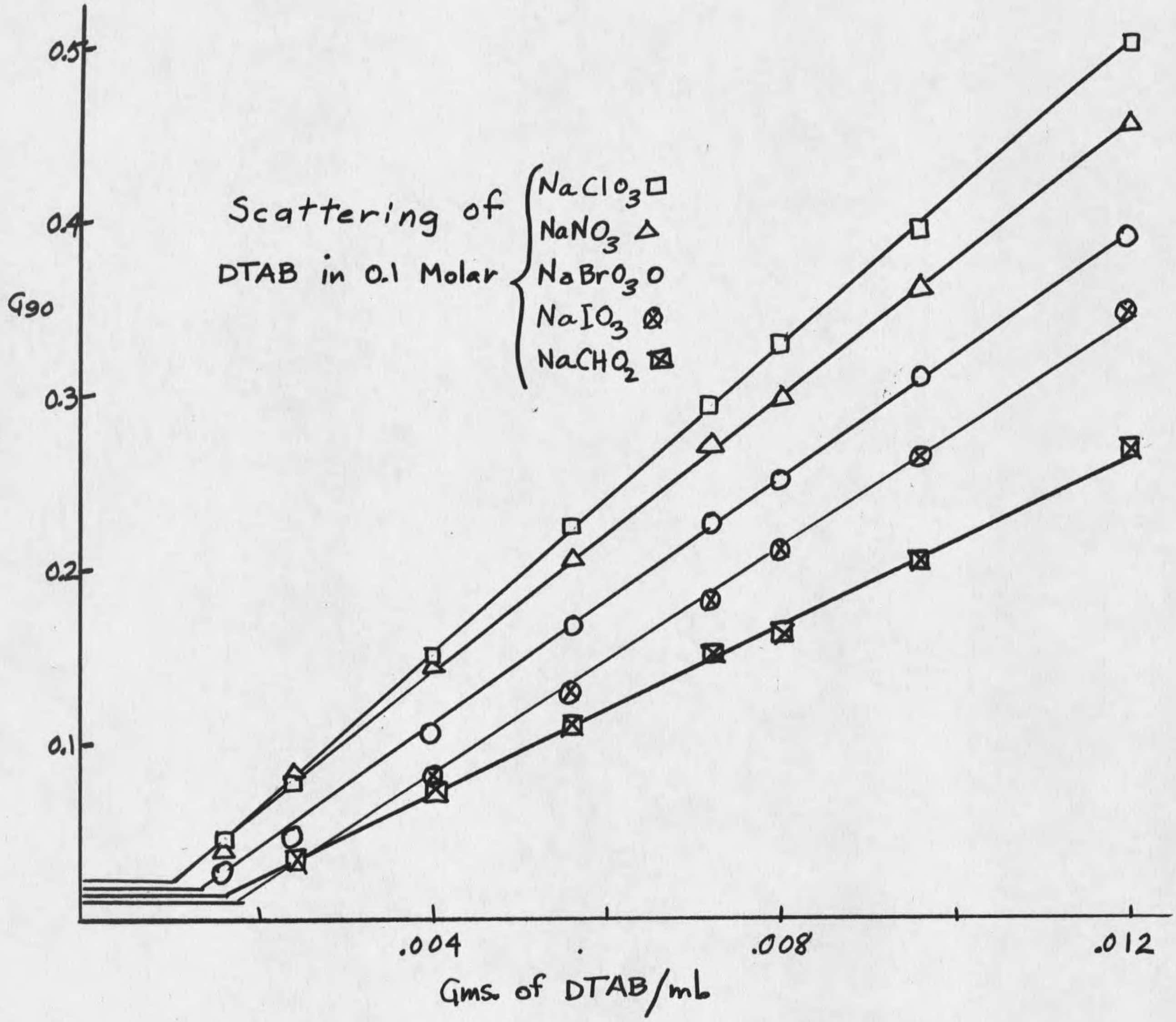

Scattering of DTAB in 0.1 Molar
NaClO$_3$ □
NaNO$_3$ △
NaBrO$_3$ ○
NaIO$_3$ ⊗
NaCHO$_2$ ⊠
G90
0.5
0.4
0.3
0.2
0.1
.004
.008
.012
Gms. of DTAB/mL

FIG. 6.

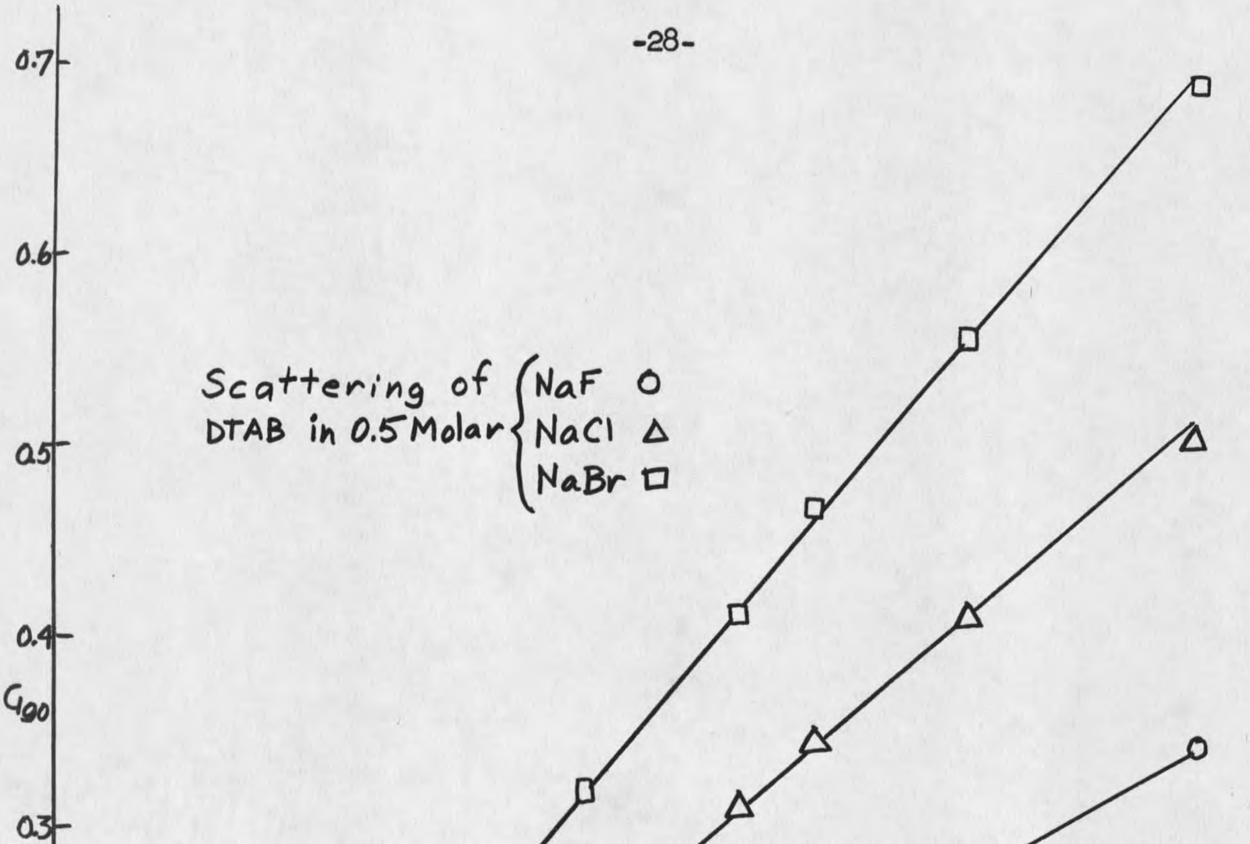

0.7
0.6
0.5
0.4
G_{90}
0.3
0.2
0.1
.004
.008
.012
Gms. of DTAB/ml.
Scattering of DTAB in 0.5 Molar
NaF ○
NaCl △
NaBr □

Fig. 7.

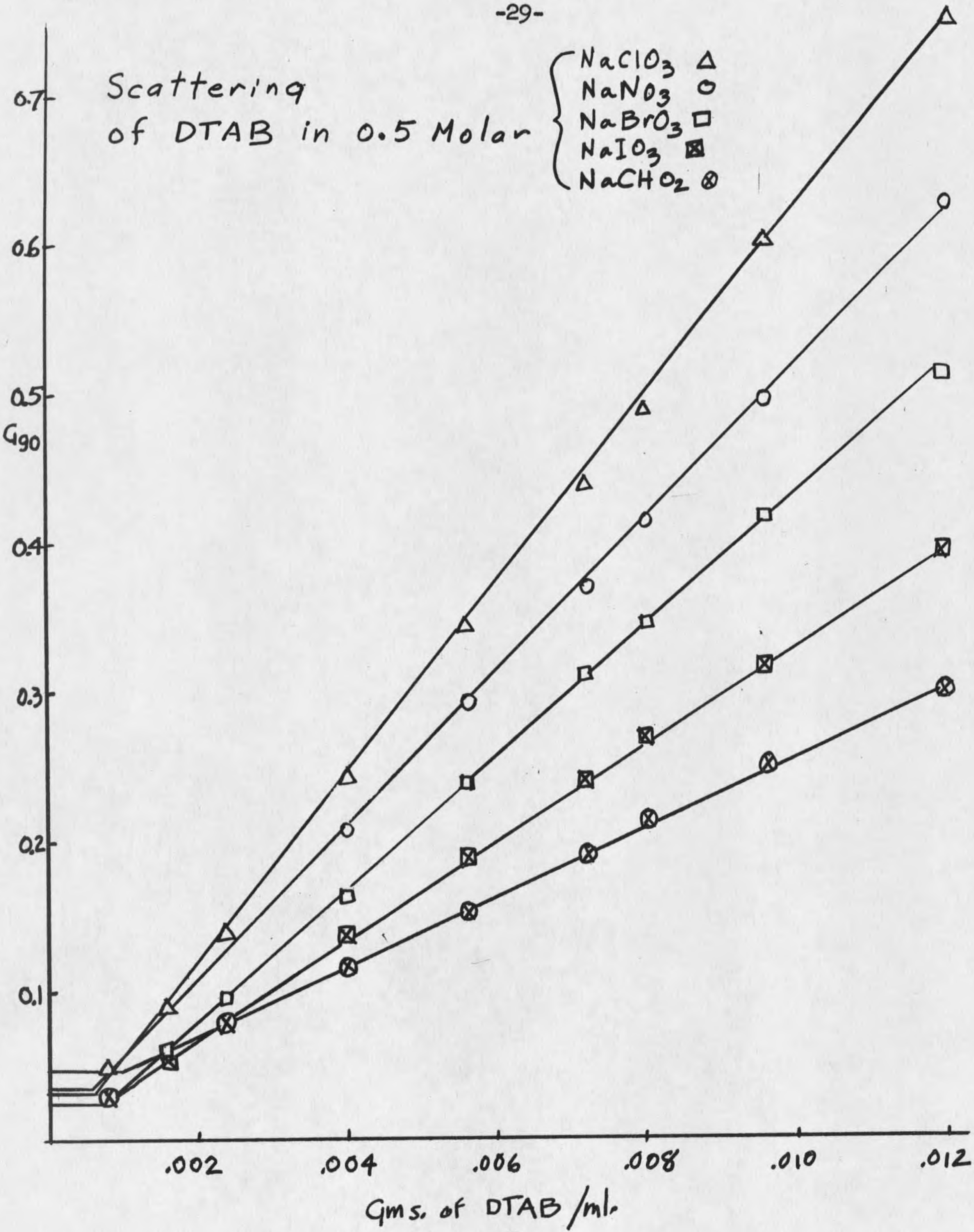

Scattering of DTAB in 0.5 Molar
NaClO3 △
NaNO3 ○
NaBrO3 □
NaIO3 ⊠
NaCHO2 ⊗
G90
0.1
0.2
0.3
0.4
0.5
0.6
0.7
.002
.004
.006
.008
.010
.012
Gms. of DTAB/ml.

Fig. 8

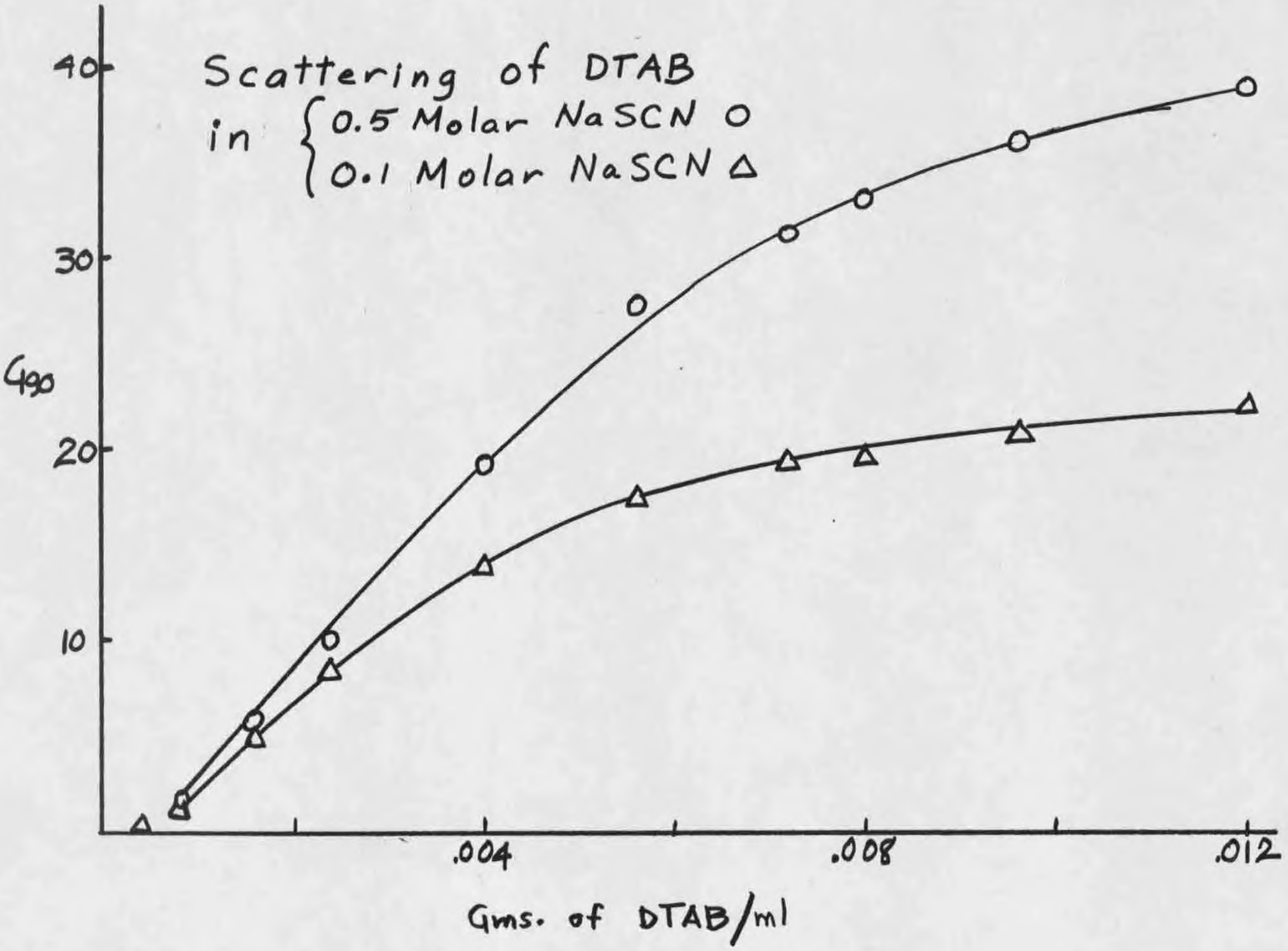
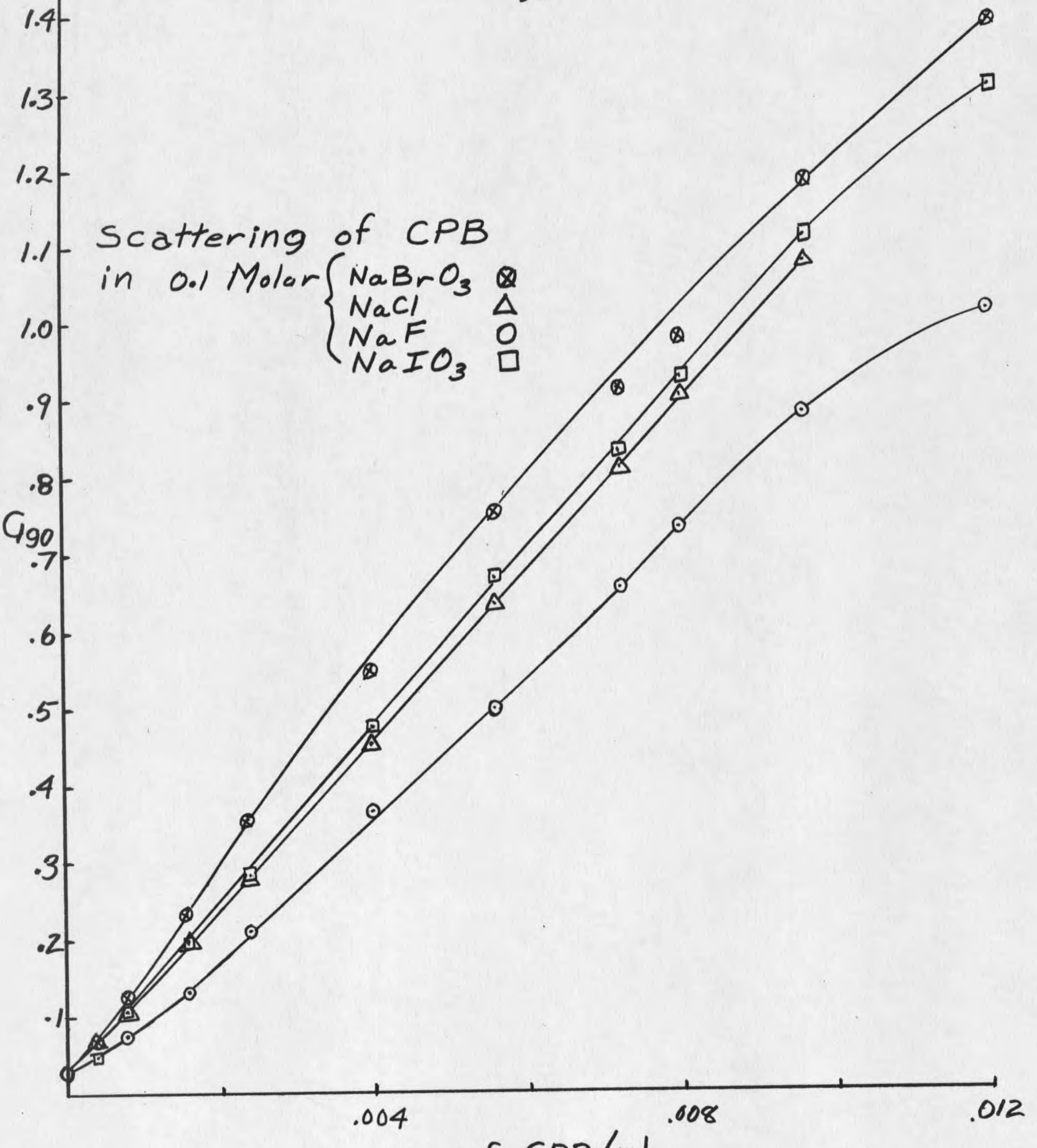

Scattering of DTAB
in { 0.5 Molar NaSCN ○
0.1 Molar NaSCN △
40
30
G_{90}
20
10
.004
.008
.012
Gms. of DTAB/ml

FIG. 9.



1.4
1.3
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
G_{90}
Scattering of CPB
in 0.1 Molar
$NaBrO_3$ ⊗
NaCl △
NaF ○
$NaIO_3$ □
.004
.008
.012
Gms. of CPB/ml.

Fig. 10

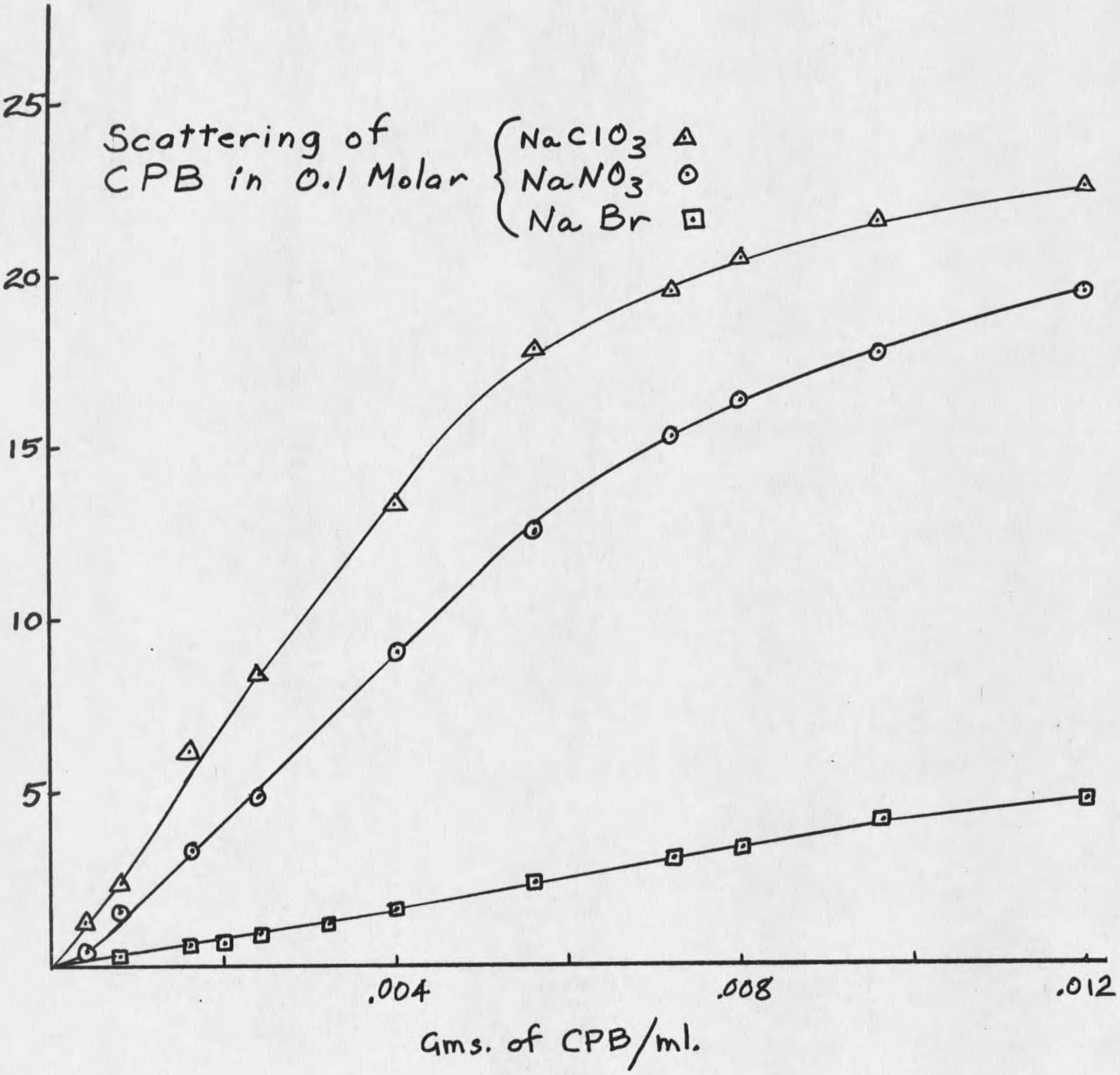

25
20
15
10
5
Scattering of CPB in 0.1 Molar
NaClO$_3$ △
NaNO$_3$ ⊙
Na Br ⊡
.004
.008
.012
Gms. of CPB/ml.

FIG. 11.

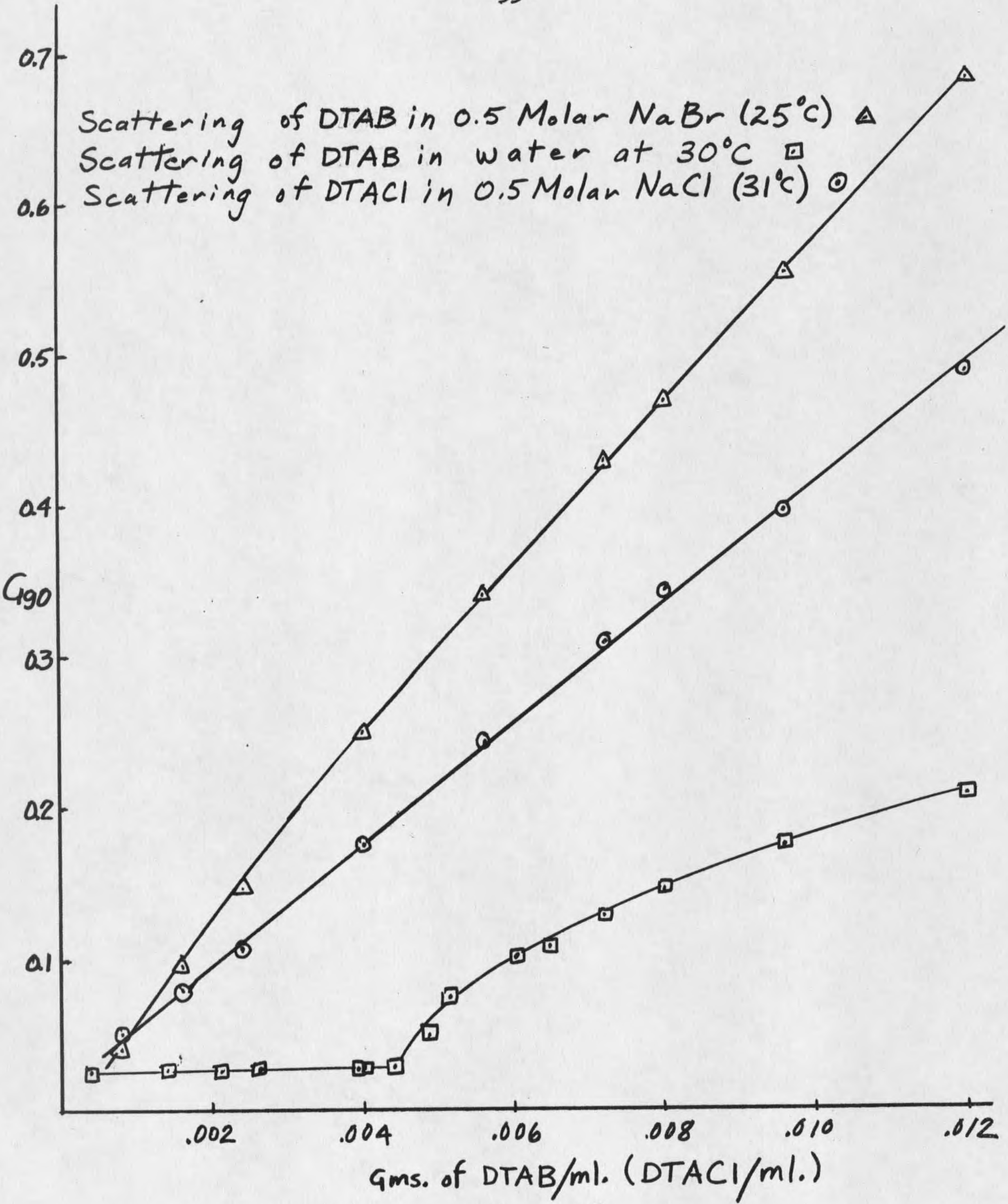

Scattering of DTAB in 0.5 Molar NaBr (25°C) △
Scattering of DTAB in water at 30°C ⊡
Scattering of DTACl in 0.5 Molar NaCl (31°C) ⊙
0.7
0.6
0.5
0.4
G_{90}
0.3
0.2
0.1
.002
.004
.006
.008
.010
.012
Gms. of DTAB/ml. (DTACl/ml.)

Fig. 12.

Tables III, IV, V and VI. Two comments with respect to some of the entries in these tables are relevant at this point. One concerns the solute species present when two different counterions appear in solution, and the other refers to qualifications applying to micellar weights obtained in some of the runs.

In those solutions containing a sodium salt other than NaBr, two different anions were available for adsorption on the micelle: the bromide ion from the DTAB or CPB and the anion X of the sodium salt. Since it was not possible to determine the exact degree of preference shown by the micelles for the various anions, computations based on three models were carried out. Two of the models represent extreme situations and computaions based upon them should therefore delineate the range of possible aggregation numbers. The models considered were:

I. Micelles which adsorb on their surfaces and attract into their immediate vicinities bromide ions to the exclusion of X anions.

II. Micelles which adsorb on their surfaces and attract into their immediate vicinities X anions to the exclusion of the bromide ions.

III. Micelles which show equal preference for bromide ions and X anions.

If S represents either the cation DTA^+ or the cation CP^+ and if B represents the anion Br^-, the surfactant formulas corresponding to the above models are respectively SB, SX, and SB_aX_b, where

$$a = [SB]/([SB] + [NaX]) \text{ and } b = [NaX]/([SB] + [NaX]).$$

Since molecular weights are computed in the light scattering technique from data extrapolated to infinite dilution -- as far as the solute

TABLE III

WEIGHTS AND AGGREGATION NUMBERS OF DODECYLTRIMETHYLAMMONIUM BROMIDE MICELLES IN 0.1 MOLAR SALT SOLUTIONS

Supporting Electrolyte	Micellar Weight		Aggregation Number	
	Model I	Models II and III	Model I	Models II and III
NaF	8,160	10,100	26.5	40.9
NaCl	11,200	11,800	36.3	44.7
NaBr	17,400	17,400	56.4	56.4
$NaNO_3$	16,800	20,500	54.5	70.6
$NaClO_3$	14,100	18,500	45.7	59.3
$NaBrO_3$	11,800	13,100	38.3	36.8
$NaIO_3$	10,500	9,100	34.0	22.6
$NaCHO_2$	7,440	9,080	24.1	33.2
NaSCN	1,660,000	14,000	5,380	4,890

TABLE IV

WEIGHTS AND AGGREGATION NUMBERS OF DODECYLTRIMETHYLAMMONIUM BROMIDE MICELLES IN 0.5 MOLAR SALT SOLUTIONS

Supporting Electrolyte	Micellar Weight		Aggregation Number	
	Model I	Models II and III	Model I	Models II and III
NaF	9,600	11,300	31.1	45.7
NaCl	14,600	15,100	47.3	57.2
NaBr	20,200	20,200	65.5	65.5
$NaNO_3$	16,700	19,800	54.2	68.2
$NaClO_3$	21,800	28,100	70.7	90.1
$NaBrO_3$	15,100	19,700	49.0	55.3
$NaIO_3$	11,600	10,900	37.6	27.0
$NaCHO_2$	8,020	9,510	26.0	34.8
NaSCN	2,000,000	1,690,000	6,490	5,900

TABLE V

WEIGHTS AND AGGREGATION NUMBERS OF CETYLPYRIDINIUM BROMIDE MICELLES IN 0.1 MOLAR SALT SOLUTIONS

Supporting Electrolyte	Micellar Weight		Aggregation Number	
	Model I	Models II and III	Model I	Models II and III
NaF	23,500	27,000	61.1	83.5
NaCl	28,100	28,600	73.1	84.1
NaBr	112,000	112,000	291	291
$NaNO_3$	657,000	777,000	1,710	2,120
$NaClO_3$	1,000,000	1,230,000	2,606	3,170
$NaBrO_3$	37,200	37,900	96.8	87.6
$NaIO_3$	30,200	28,200	78.6	58.8

TABLE VI

MICELLAR WEIGHTS AND AGGREGATION NUMBERS IN CHECK SYSTEMS

System	Micellar Weight	Aggregation Number
DTAB in water at 30° C.	16,200	52.5
DTAB in 0.5 molar NaBr at 25° C.	21,400	69.4
DTACl in 0.5 molar NaCl at 32° C.	14,900	56.7

particles are concerned -- the molarity of SB, [SB], used to calculate an a and b for a run was taken as the critical micelle concentration. At the critical micelle concentration $[X] \gg [B]$. Consequently, models II and III should give results which do not differ appreciably and which are closer to the actual value than one based on model I.

As may be noted in Tables III, IV and V, some of the computed molecular weights are in excess of 100,000 and that one -- for DTAB in 0.5 molar NaSCN -- approaches 2,000,000. The systems giving these high values are visibly turbid and undoubtedly exhibit dissymmetry, i.e., do not scatter light symmetrically about 90°. Dissymmetry arises when the scattering particles are so large (have at least one dimension that exceeds 1/20th of the wave length of the exciting radiation) that they can not be treated as single dipoles, but must be considered as an array of dipoles. Less light is scattered in the backward direction than in the forward because of interference effects.

Molecular weights can be corrected for dissymmetry if the extent of the dissymmetry is known. With the instrument used in this investigation, one is restricted to measurements at 90° and so no corrections are possible. Since the light scattered at 90° for a large particle is less than what it would be if interference effects were absent, the calculated molecular weight will be too small. For this reason the high molecular weights reported in the tables must be regarded as minimum values.

In Table VI are given the results of three determinations carried out for check purposes. The first two runs listed were made to check the purity of the DTAB used in the investigation. Literature values for the micellar weight of DTAB in water run all the way from 12,200 (34) to 19,200 (36). The turbidity plot corresponding to the 19,200 value shows marked curvature in the vicinity of the critical micelle concentration and may be ignored for this reason. The DTAB used obviously contained an impurity. The low value of 12,200 as obtained by Tartar indicates that either his material was the purest examined or that calibration errors exist. Because our material exhibits no turbidity curvature at the critical micelle concentration and because its critical micelle concentration agrees with that of Tartar's, we have assumed that its purity was sufficient for the purpose for which we used it.

The DTACl run was made to see if our procedure of using DTAB with NaX produced the same result that would have been obtained had DTAX been available and used. As can be seen from Table IV, the DTAB in the 0.5 molar NaCl run resulted in a micellar weight of 15,100 and an aggregation number of 57.2 (models II and III). These values are in very close agreement with those obtained in the DTACl in 0.5 molar NaCl run and given in Table VI. The indication is that our procedure is sound.

Table VII summarizes the refractive index work. Each entry in the second column represents the average of at least three independent determinations. Gradients for surfactants in the second column refer to constant supporting electrolyte molarity between surfactant solution and solvent. Within the number of significant figures reported, these gradients were found to be concentration independent. The gradients in the third and fourth column were computed from those in the second by an unpublished method due to Anacker. They refer to constant supporting

REFRACTIVE INDEX GRADIENTS IN LITER-MOLE^{-1}

$\lambda = 4358Å$, 32° C.

Solute	$\Delta n/c$	$\Delta n/c$(0.1m NaX)	$\Delta n/c$(0.5m NaX)
NaF	.0054		
NaCl	.0104		
NaBr	.0146		
$NaNO_3$	.00965		
$NaClO_3$	.0101		
$NaBrO_3$	.0165		
$NaIO_3$	.0263		
$NaCHO_2$	.00882		
NaSCN	.0179		
DTAF	.0373	.0372	.0366
DTACl	.0419	.0416	.0405
DTAB	.0466	.0462	.0444
$DTANO_3$	.0410	.0407	.0396
$DTAClO_3$	.0409	.0406	.0393
$DTABrO_3$	.0478	.0472	.0449
$DTAIO_3$	.0578	.0567	.0525
$DTACHO_2$	.0396	.0394	.0384
DTASCN	.0489	.0484	.0463
CPF	.0550	.0548	
CPCl	.0601	.0597	
CPB	.0646	.0640	
$CPNO_3$	.0578	.0574	
$CPClO_3$	.0585	.0581	
$CPBrO_3$	.0679	.0672	
$CPIO_3$	.0752	.0739	

electrolyte molality between surfactant solution and solvent. Micellar weights were computed with their use. As can be seen from the table, they are dependent on supporting electrolyte concentration.

A remark or two may be in order concerning the method used to calculate the $\Delta n/c$ value for a surfactant SX, which had not been prepared. A solution of SB and NaX with respective molarities of s and x was regarded as containing SX of concentration s and $NaB_{s/(s+x)}X_{x/(s+x)}$ of concentration x. The difference in refractive index between this solution and one s molar in NaBr and (x-s) molar in NaX when divided by s was taken as $\Delta n/c$ for SX.

The H value corresponding to a surfactant species SB_aX_b was taken as $\frac{s}{s+x}H_{SB} + \frac{x}{s+x}H_{SX}$ where H_{SB} and H_{SX} are the respective H values of SB and SX.

DISCUSSION

For background purposes we shall briefly review some of the fundamentals behind micelle formation. Surfactant ions are partially hydrophilic because of their polar heads and partially hydrophobic because of their hydrocarbon tails. These conflicting natures are satisfied simultaneously in solution through the formation of aggregates, the ionic heads making up the surface and the paraffin chains the interior. In this way the polar groups maintain contact with the solvent and hydrocarbon tails escape from it.

As far as the micelles themselves are concerned, two types of opposing forces must be considered: the short range attractive forces (van der Waals' forces) between paraffin chains and the long range repulsive forces (Coulombic forces) between polar heads. The former are essentially independent of micelle size while the latter increase with the aggregation number. Initially as the chains come together the van der Waals' forces predominate and the micelles can increase in size. Eventually the two types of force come into balance and micelle size is stabilized.

Both the short range and the long range forces may be altered and the equilibrium micelle size shifted. If, for example, the hydrocarbon chain of a surfactant ion is lengthened, the van der Waals' attractive forces will increase. This alteration should lead to an increase in micelle size. Anacker (1) studied the series: decyl-, dodecyl-, tetradecyl-, hexadecyltrimethylammonium bromide in 0.0130 M. KBr. The respective aggregation numbers for these surfactants were determined to be 38, 56, 95, and 170, thus in agreement with the prediction.

The Coulombic forces may be altered by the addition of inorganic salts. Experimentally it has been observed that this action results in an increase of micellar size. The salt reduces the thickness of a micelle's ionic atmosphere and thus screens the action of the charges on the micelle. The electrical work required to bring the polar group of a surfactant ion from the body of the solution to the surface of the micelle is decreased with the result that the equilibrium size of the micelle is displaced upwards.

Let us now consider the results of the present investigation. For the three sets of experiments, the aggregating powers of the counterions increase in the orders (Model II):

DTAB in 0.1 M. NaX: IO_3^-, CHO_2^-, BrO_3^-, F^-, Cl^-, Br^-, ClO_3^-, NO_3^-, CNS^-.

DTAB in 0.5 M. NaX: IO_3^-, CHO_2^-, F^-, BrO_3^-, Cl^-, Br^-, NO_3^-, ClO_3^-, CNS^-.

CPB in 0.1 M. NaX: IO_3^-, F^-, Cl^-. BrO_3^-, Br^-, NO_3^-, ClO_3^-.

Precipitation was caused by $C_2H_3O_2^-$, ClO_4^-, and I^-.

Colloidal chemists will immediately recognize in these arrangements a striking similarity to the lyotropic, or Hofmeister, series of anions. According to the quantitative characterixation of Bruins (5), the series follows the order:

F^-, IO_3^-, BrO_3^-, Cl^-, ClO_3^-, Br^-, NO_3^-, ClO_4^-, I^-, CNS^-. The formate and acetate ions do not appear in Bruins' list.

The lyotropic series denotes the order of relative effectiveness of the anions in influencing various phenomena, such as the swelling of starch granules, the gelation of sols, the liquefaction of gels, the effect of ions on the viscosity of sols, the coagulation of sols, and ion exchange with colloidal particles. The lyotropic series is encoutered in strictly physical chemical phenomena, such as the solubility of gases in solutions of electrolytes, the catalysis of chemical reactions by ions, the effects of ions on the surface tension of water, and the displacement of the temperature of maximum density of water. Since colloids are not involved in these last examples, the series must be a consequence of the inherent properties of the ions and not of some peculiarity of the colloidal state. Exceptions often occur in the series and the order for any one phenomenon may change with concentration.

No completely satisfactory explanation of the series exists. Pauli and Valko (25) ascribed the order to the respective sizes of the anhydrous ions. This explanation can not be correct; from left to right size increases for the halides but decreases for IO_3^-, BrO_3^-, and ClO_3^-.

Cooper (7) has attempted to show that there is a relationship between an ion's position in the series and its free energy of formation. A number of exceptions spoil the correlation. The free energies of formation of complex ions are related to processes not involved in any of the phenomena being considered, and it is therefore difficult to see how they could explain the series in any event.

An excellent correlation between the heat of hydration of an ion and its position in the lyotropic series exists. Since lyotropic effects occur in non-aqueous surroundings, however, any theory which deals only with the interaction of the ions with the solvent can not be general.

In Voet's opinion (38) "…. lyotropic series are caused by different ionic field strengths." He supports his view by stressing the fact that ionization potentials for cations bear a linear relationship to the lyotropic numbers of the cations. Unfortunately not enough electron affinity data are available to test this view with respect to anions.

It seems likely that the degree of an anion's interaction with water is an important factor in determining its relative aggregating power as far as the present work is concerned. If no hydration occurred, one would predict that the smaller the ion, the stronger its adsorption and the larger the equilibrium size of the micelle. The halide ion sequence is in disagreement with this prediction and hydration effects must therefore be significant. According to the ionic heats of hydration data, F^-

would be the most strongly hydrated and I^- the least. The IO_3^-, BrO_3^-, ClO_3^- sequence could be explained solely on a size basis. This does not rule out the possibility of hydration effects, however. For these three ions the degree of hydration increases with the size and the two factors work together. According to Rice the IO_3^- probably becomes $I(OH)_6^-$ in aqueous solution, whereas the BrO_3^- and ClO_3^- take on at most one molecule of water.

There is strong evidence to indicate that the formate ion, which has a very low aggregating power, strongly interacts with water. Formic acid has an ionization constant of about 2×10^{-4}, which would indicate that the formate ion undergoes appreciable hydrolysis. Since formic acid molecules are known to dimerize through hydrogen bonding, there is the strong possibility of hydrogen bonding with water.

The perchlorate ion as one of the highest aggregating powers of the ions studied. Because of its relatively large size and symmetrical structure (tetrahedral), its degree of hydration is presumably zero or close to it. Its relatively low hydration energy is consistent with this picture and the ClO_4^- can cause the precipitation of $DTAClO_4$ and $CPClO_4$ through adsorption on the micellar surfaces.

Hydration effects can not tell the whole story. Whenever the acetate ion is listed in a version of the lytropic series it comes before Cl^-. Its action in causing precipitation is therefore unexpected. If the lyotropic series as given by Bruins were strictly followed, the ClO_4^- and I^- ions should have exhibited smaller aggregating powers than CNS^-. This was not the case. Obviously other factors than hydration are operating. At the present time we can only speculate as to what these might be.

SUMMARY

The accomplishments of the investigation may be summarized as follows:

1. A 90° light scattering instrument was designed, constructed, and calibrated.

2. The turbidities of solutions of dodecyltrimethylammonium bromide in 0.1 and 0.5 molar solutions of various supporting electrolytes ($NaCHO_2$, NaF, NaCl, NaBr, $NaIO_3$, $NaBrO_3$, $NaClO_3$, $NaClO_4$, and $NaNO_3$) were measured.

3. The turbidities of solutions of cetylpyridinium bromide in 0.1 molar solutions of various supporting electrolytes (NaF, NaCl, NaBr, $NaIO_3$, $NaBrO_3$, $NaClO_3$, and $NaNO_3$) were measured.

4. Refractive index increments were measured for various solutions of the two surfactants mentioned above and used to compute refractive index gradients of other surfactants differing only in the counterion.

5. Micellar weights and aggregation numbers were computed for various assumed solute species.

6. The aggregating powers of the various anions studied were found to increase in a manner roughly consistent with the lytropic series of anions.

7. The possibility that the magnitude of an anion's aggregating power is intimately related to its hydration energy was discussed and suggested.

8. The prior observations of other workers in the field that added

salt increases micellar weight and lowers the critical micelle concentration were confirmed.

9. A number of solutions examined were found to be visibly turbid and to contain micelles with weights approaching 2,000,000. These solutions provide support for the growing conviction that the Hartley spherical model for the micelle can not explain all surfactant solution phenomena.

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VITAE

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In May, 1949, he received his B. S. degree in physics, chemistry and mathematics from Bihar National College, Patna, India.

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He went to Montana State College, Bozeman, Montana, to do his graduate work in 1955.

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