LIGHT SCATTERING BY ELECTROLYTE SOLUTIONS CONTAINING CHARGED COLLOIDAL PARTICLES

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ABSTRACT

A brief survey is given of light scattering equations for multicomponent systems, based on fluctuation theory. The equations are specialized for the case of one low molecular weight electrolyte, one colloidal electrolyte and solvent. The importance of the negative absorption of the low molecular weight electrolytes unto the colloidal particles is stressed. It is shown how analytical and optical data relating to this effect can be derived from Donnan equilibria.

The theory is applied to light scattering data for polymethacrylic acid solutions and to micellar solutions of sodium dodecylsulfate.

A method is developed to interpret light scattering data without the use of Donnan equilibria. This method is based upon the idea that a change of the low molecular weight co-ion does not affect the structure of the electrical double layer and thus does not affect negative adsorption. By using a variety of co-ions extrapolation is then possible to a low molecular weight salt with zero refractive index increment.

INTRODUCTION

The measurement of scattered light has for a long time been a tool of great importance in colloid science and in the field of large molecules. In the early days of colloid science "Tyndall light" was used as an indication of the colloidal state. With the ultramicroscope in the hands of Siedentopf and Zsigmondy (1903) Tyndall scattering was resolved into contributions from individual particles and used to count particles or follow their Brownian motion, electrophoresis and the like. Later, particularly after the publications by Putzeys and Brosteaux (1935) and by Debye (1944), it was realized that the intensity of the scattered light from a two-component solution allowed the calculation of the molecular weight of the solute.

Equations for the intensity of scattered light can be derived in two rather different ways. The first method considers the scattering by individual particles (Rayleigh, 1871), the second considers fluctuations in concentrations in small volumes of the solution and the scattering by these fluctuations (Smoluchowski, 1908; Einstein, 1910).

For a system with more than two components, both methods of calculation have to be applied with caution. As a rule the system will not be a completely random mixture of the component molecules. Forces of attraction and repulsion between molecules cause positive or negative adsorption, the formation of complexes, etc. In the application of the Rayleigh method these aggregates, rather than the individual particles have to be considered as the scattering units. In the fluctuation method it has to be taken into account that some of the fluctuations are correlated instead of random.

In electrolyte systems these effects may be particularly important because electrostatic forces are strong and far reaching.

LIGHT SCATTERING EQUATIONS DERIVED BY FLUCTUATION METHOD

In the fluctuation method, the turbidity τ of a solution is given by Einstein (1910)

$$\tau = \frac{32\pi^3 \bar{n}^2 \overline{(\Delta n)^2} V}{3\lambda_0^4} \qquad (1)$$

where $\Delta n = n - \bar{n}$, n is the index of refraction in a volume V, $\bar{n}$ the average index of refraction, and λ_0 the wavelength of the light *in vacuo*. A prerequisite for the validity of equation (1) is that $\overline{(\Delta n)^2} V$ is independent of the size of the volume chosen. Moreover, V should be small compared to the wavelength, in order that phase differences in the light waves are negligible in this volume.

For small fluctuations, $\overline{(\Delta n)^2}$ can be written

$$\overline{(\Delta n)^2} = \sum_{i,k=0}^{m} (\partial n/\partial N_i)_{NVT} (\partial n/\partial N_k)_{NVT} \overline{\Delta N_i \Delta N_k} \qquad (2)$$

where N_j is the number of molecules of type j in the volume V and ΔN_j the fluctuation in this number. In the partial differentiations V, T and all N_j's except the one used in the differentiation are kept constant. The components of the system are numbered 0 (solvent), 1, ... , m.

Zernike (1915) has used the grand canonical ensemble to derive the following expression for $\overline{\Delta N_i \Delta N_k}$.

$$\overline{\Delta N_i \Delta N_k} = kT(\partial \bar{N}_i/\partial \mu_k)_{\mu V T} = kT(\partial \bar{N}_k/\partial \mu_i)_{\mu V T} \qquad (3)$$

where μ_j is the chemical potential of component j.

Although the turbidity can now be expressed with the aid of equations (1), (2) and (3) in macroscopic properties of the system it remains awkward that:

(1) The derivatives $\partial n/\partial N_j$ are taken at constant volume. It would be more convenient to convert them to $(\partial n/\partial c_j)_P$ or $(\partial n/\partial g_j)_P$ where c_j and g_j are the concentrations in moles per unit volume or in grams per unit volume respectively.

(2) In colloidal systems the components are as a rule very different in nature and in concentration. It is therefore convenient to split the turbidity as far as possible into contributions from the solvent, from the low molecular weight solutes and from the colloidal components. In the present article we shall limit ourselves to a single colloidal component.

(3) In equation (3) the system is described with the variables μ, V and T. It is preferable to convert these into μ_0, N_1, μ_2 ... μ_m, P and T when component 1 is the colloid.

Brinkman and Hermans (1949) carried out the conversion from V to P as the parameter to be kept constant, they separated the contribution of the solvent from that of the other components, and instead of the $(\partial N/\partial \mu)$'s in equation (3) they used the more familiar $(\partial \mu/\partial N)$'s.

Ooi (1958) separated the contribution of the colloid from that of all other components for the case of a neutral colloid in a mixture of low molecular weight solvents.

Casassa and Eisenberg (1960, 1961) and two of the present authors (Vrij, 1959; Vrij and Overbeek, 1962) treated the case of a charged colloid (polyelectrolyte) in an electrolyte solution. The same problem has been treated in somewhat different ways by a number of authors (Schönert, 1961; Strazielle and Benoit, 1961; Ullmann and Benoit, 1962, and Stigter, 1960).

We will not repeat these derivations in detail but just give the most important equations and refer for the derivations to the papers just mentioned, in particular to Vrij and Overbeek (1962).

The final equations are

$$\tau - \tau' = \frac{32\pi^3 \bar{n}^2 kT}{3\lambda_0^4} \frac{\left[\sum\limits_{i=1}^{m} \gamma_i(\partial c_i/\partial c_1)_{\mu_s,T}\right]^2}{(\partial\Pi/\partial c_1)_{\mu_0,\mu_2...\mu_m,T}} c_1 \tag{4}$$

$$\tau' = \frac{32\pi^3 \bar{n}^2 kT}{3\lambda_0^4} \left\{\left[V^2\left(\frac{\partial n}{\partial V}\right)_{N,T}^2 - \left(\sum\limits_{i=1}^{m} \gamma_i c_i\right)^2\right]\kappa + \sum\limits_{i,k=2}^{m} \gamma_i\gamma_k(\partial c_i/\partial \mu_k)_{\mu_s \neq \mu_k}\right\} \tag{5}$$

$$\gamma_i = (\partial n/\partial c_i)_{P,T,c}$$

where the subscript μ_s indicates that the chemical potentials of all low molecular weight components are kept constant. Π is the osmotic (= Donnan) pressure difference between the colloidal solution and a solution containing the low molecular weight components only in equilibrium with it.

The contribution τ' is very nearly equal to the turbidity of the electrolyte solution with colloid concentration zero (see Vrij and Overbeek, 1962) and can thus be measured directly. The term $(\partial\Pi/\partial c_1)$ is derived via the Gibbs–Duhem equation from a term $(\partial\mu_1/\partial N_1)_{V,\mu \neq \mu_1} = (\partial N_1/\partial\mu_1)_{V,\mu \neq \mu_1}^{-1}$

For a two-component system (solvent 0 and colloid 1), using equation (7) for the conversion to concentration by weight

$$g_i = c_i/M_i \tag{7}$$

where M_i is the molecular weight of component i, and equation (8) for the osmotic pressure

$$\Pi = RTc_1 + B'c_1{}^2 = \frac{RT}{M_1}g_1 + Bg_1{}^2 \tag{8}$$

where B is the second virial coefficient, equation (4) can be written

$$\frac{32\pi^3\bar{n}^2(\partial n/\partial g_1)^2_{P,T}}{3\lambda_0{}^4 N_A(\tau - \tau')}g_1 = \frac{1}{M_1} + \frac{2B}{RT}g_1 \tag{9}$$

τ' is with high approximation equal to the turbidity of the solvent, and N_A is Avogadro's number.

In a multicomponent system, with one high molecular weight component, equation (8) still describes the osmotic pressure (membrane permeable to all low molecular weight components) correctly, even if the system contains electrolytes. In the last named case Π is the Donnan pressure. But the term $\sum \gamma_i(\partial c_i/\partial c_1)$, which replaces $(\partial n/\partial c_1)$ in the simple system introduces the influence of adsorption (and of correlated fluctuations). This term can be treated in two different ways. All $\gamma_i = \partial n/\partial c_i$ can be measured separately and $(\partial c_i/\partial c_1)_{\mu_s}$ can be determined analytically in a membrane equilibrium. $(\partial c_i/\partial c_1)_{\mu_s}$ represents the amount of component i to be added to the system per mole of component 1 in order to keep μ_s constant: i.e. to keep the system in equilibrium with the Donnan equilibrium liquid.

Another possibility depends on equation (10), which is a very good approximation (Vrij, 1959)

$$\sum_{i=1}^{m} \gamma_i(\partial c_i/\partial c_1)_{T,\mu_s} = (\partial n/\partial c_1)_{T,\mu_s} \tag{10}$$

The whole sum can be measured directly by determining the change in index of refraction of the inner liquid in a Donnan membrane equilibrium upon addition of one mole of component 1 per unit volume.

So far the whole treatment has been based on the use of thermodynamically valid, i.e. electroneutral components. Evidently this does not leave space for non-electroneutral fluctuations. It should therefore be investigated whether such non-neutral fluctuations can contribute measurably to the turbidity. Hermans (1949, 1950) has shown that in volume elements with linear dimensions larger than the Debye–Huckel length $(1/K)$

$$\frac{1}{K} = \sqrt{\left(\frac{DRT}{4\pi F^2 \sum z_i{}^2 c_i}\right)} \tag{11}$$

where D is the dielectric constant, F the Faraday and z_i and c_i the valence and concentration of the i-ions in moles per unit volume, non-electroneutral fluctuations contribute to a negligible extent to the turbidity. In aqueous solutions more than 10^{-3} M the error from non-electroneutral fluctuations is smaller than 1 per cent for visible light.

If we limit our considerations now to a system composed of solvent (0), colloidal electrolyte (1) and one low molecular weight electrolyte (2), equation (4) can be written

$$\frac{Hg_1}{\tau - \tau'} = \frac{1}{M_1^*} + \frac{2B^*}{RT} g_1 \qquad (12)$$

with

$$H = \frac{32\pi^3 n^2 (\partial n / \partial g_1)^2_{g_2}}{3\lambda_0^4 N_A} \qquad (13)$$

and

$$M_1^* = M_1 \left[1 + \frac{(\partial n / \partial g_2)_{g_1}}{(\partial n / \partial g_1)_{g_2}} \left(\frac{\partial g_2}{\partial g_1} \right)_{\mu_s} \right]^2 \qquad (14)$$

and

$$B^* = B \left[1 + \frac{(\partial n / \partial g_2)_{g_1}}{(\partial n / \partial g_1)_{g_2}} \left(\frac{\partial g_2}{\partial g_1} \right)_{\mu_s} \right]^{-2} \qquad (15)$$

Furthermore

$$(\partial n / \partial g_1)_{\mu_2} = (\partial n / \partial g_1)_{g_2} \left[1 + \frac{(\partial n / \partial g_2)_{g_1}}{(\partial n / \partial g_1)_{g_2}} \left(\frac{\partial g_2}{\partial g_1} \right)_{\mu_s} \right] \qquad (16)$$

Relations equivalent to these have been used by Stockmayer (1950) and by Ooi (1958), whereas more recently Strauss and Wineman (1958) used the equivalent of equation (14) in determining the molecular weight of polyphosphate.

In equations (12)–(15) $(\partial n / \partial g_i)$ is a conventional refractive index increment. $\partial g_2 / \partial g_1$ represents the adsorption of the salt to the colloidal electrolyte and is negative (if specific adsorption is absent) on account of the repulsion of the co-ions by the charged particle. For low charge densities and high electrolyte contents half of the charge on the particles is compensated by excess counterions and half by the deficit of co-ions. For higher charge densities and lower electrolyte concentrations the compensation of the charge shifts more to the counterions.

INCOMPLETE DISSOCIATION OF THE COLLOIDAL COMPONENT

In the approach outlined above the negative adsorption is derived from experimental data, without the use of a model for the constitution of the solution. Mysels (1955) and Princen and Mysels (1957) and Prins and Hermans (1956) have introduced the assumption of ideal behavior of the

solution except for incomplete dissociation of the colloidal electrolyte. In that case simple Donnan theory can be applied to calculate corrections to the light scattering molecular weight comparable to our equation (14) and a value can be given for the second virial coefficient. If the degree of dissociation is α and the valency of the polyelectrolyte is equal to z, the correction for the molecular weight assumes the form

$$M_1^* = M\left[1 - \tfrac{1}{2}z\,\frac{M_2}{M_1}\frac{(\partial n/\partial g_2)_{g_1}}{(\partial n/\partial g_1)_{g_2}}\right]^2 \tag{17}$$

corresponding to a negative adsorption of $\tfrac{1}{2}\alpha z$ moles of salt per mole of polyelectrolyte.

In the same picture the main contribution to the second virial coefficient becomes

$$\frac{2B}{RT} = \frac{\alpha^2 z^2}{2c_2 M_1^2} \tag{18}$$

In principle it is then possible to use the second virial coefficient to determine α and to use this α for the correction factor in equation (17). According to calculations made by one of us (Vrij, 1959), this procedure although qualitatively correct underestimates the correction in equation (14) or (17) by a factor 1.5–3.0 depending on the electrolyte content.

APPLICATIONS

Polymethacrylic Acid

The principle described above is well illustrated by a series of measurements of light scattered by solutions of polymethacrylic acid (PMA) and its salt in different electrolyte solutions. For experimental details see Vrij and Overbeek (1962).

For one series of measurements the polyacid was dissolved in 0.045 M HCl thus suppressing dissociation nearly completely. Polyelectrolyte effects are absent. The second virial coefficient is very low, also indicating negligible interaction between the polyacid molecules.

For the other measurements PMA was half neutralized with NaOH and dissolved in a variety of electrolyte solutions. The second virial coefficient is high in all cases due to repulsion between the polyelectrolyte molecules. Refractive index increments were determined for the salts, for the polymer at constant salt concentration and for the polymer in a Donnan membrane equilibrium i.e. at constant chemical potential of the salt.

These data can now be used in a number of different ways.

(a) The refractive index increment at constant μ as determined in the Donnan equilibrium can be used directly in the light scattering equations. Then M_1

and B can be determined from a plot of $H'g_1/(\tau - \tau')$ against the concentration g_1 where

$$H' = \frac{32\pi^3 n^2 (\partial n/\partial g_1)_{\mu_s}^2}{3\lambda_0^4 N_A} = H \frac{(\partial n/\partial g_1)_{\mu_s}^2}{(\partial n/\partial g_1)_{g_2}^2} \tag{19}$$

It is also possible to determine M_1^* and B^* according to equation (12) first from the more usual plot of $Hg_1/(\tau - \tau')$ against g_1 (see Fig. 1), applying
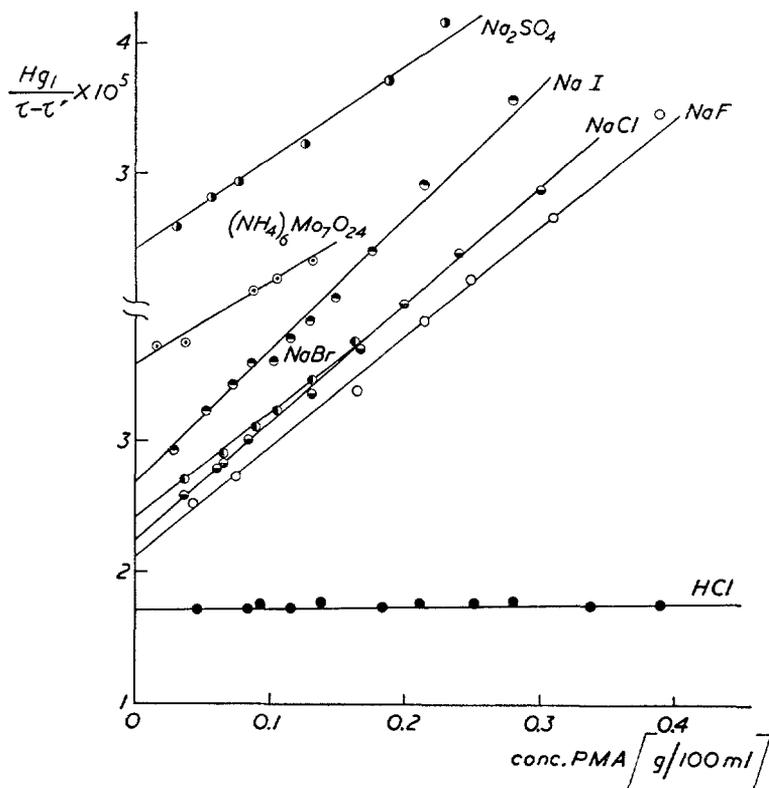
FIG. 1. $Hg_1/(\tau - \tau')$ plotted against concentration PMA. The data for Na_2SO_4 have been shifted upwards for clarity.

the correction factor of H in equation (19) afterwards. The results thus obtained are given in Tables 1 and 2.

The values of M_1^* and B^* are different for each of the salts. The true molecular weight found from the different salt solutions appears to be $51,000 \pm 1000$. The second virial coefficients, B, for the different halides are nearly identical, indicating that the interactions between pairs are also very similar.

TABLE 1. REFRACTIVE INDEX INCREMENTS OF SALT AND OF PMA AT 20°C*

Solvent	$M_2(\partial n/\partial g_2)_{g_1}$ [ml/mole]	$(\partial n/\partial g_1)_{g_2}$ [ml/g]	$(\partial n/\partial g_1)_{\mu_2}$ [ml/g]	$\dfrac{\partial(g_2/M_2)}{\partial(g_1/E_1)}$
0.045 M HCl	—	0.156	0.162	positive
0.1 M NaF	5.5	0.229 ⎤	0.219	−0.28
0.1 M NaCl	10.2	—	0.213	−0.25
0.1 M NaBr	13.4	0.234 ⎱ Av.	0.209	−0.24
0.1 M NaI	21.2	— ⎰ 0.228	0.197	−0.25
0.1 M Na₂SO₄	21.3	—	0.210	−0.14⁵
0.01 M (NH₄)₆Mo₇O₂₄	—	0.227 ⎦	0.169	

* The polymer in the salt solutions is half neutralized; concentrations g_1 are expressed in gram PMA (acid form) per milliliter. E_1 is the equivalent weight of half neutralized PMA ($E_1 = 172$).

TABLE 2. APPARENT AND TRUE MOLECULAR WEIGHT AND SECOND VIRIAL COEFFICIENT OF PMA

Solvent	$M_1^* \times 10^{-3}$	$M_1 \times 10^{-3}$	$B^* \times 10^3$ [ml/g]	$B \times 10^3$ [ml/g]
0.045 M HCl	58.0	53.8	0	0
0.1 M NaF	46.7	51.5	4.12	3.74
0.1 M NaCl	44.7	52.1	4.35	3.73
0.1 M NaBr	41.2	50.0	4	3.3
0.1 M NaI	37.2	50.7	5.00	3.66
0.1 M Na₂SO₄	41.5	49.8	3.42	2.85
0.01 M (NH₄)₆Mo₇O₂₄	28	52	2.95	1.59

(b) A combination of $(\partial n/\partial g_1)_{\mu_2}$ and $(\partial n/\partial g_1)_{g_2}$ can be used to determine the (negative) adsorption of the salt using equation (16). This has been done using an average value of 0.228 ml/g for $(\partial n/\partial g_1)_{g_2}$ for the half neutralized polymer and individual values for $(\partial n/\partial g_1)_{\mu_2}$.

It is preferable to compare the adsorptions on an equivalent weight basis rather than on a weight basis. Therefore equation (16) is modified into

$$(\partial n/\partial g_1)_{\mu_2} = (\partial n/\partial g_1)_{g_2} + (\partial n/\partial g_2)_{g_1} \frac{M_2}{E_1} \frac{\partial(g_2/M_2)}{\partial(g_1/E_1)} \qquad (20)$$

where M_2 is the formula weight of the salt and E_1 the equivalent weight of the half neutralized polymer ($E_1 = 172$). Results are given in the last column of Table 1, but are not very accurate.

(c) A presumably more accurate value of the negative adsorption is found by assuming that it has the same value in the four sodium halide solutions. If then $(\partial n/\partial g_1)_{\mu_2}$ is plotted against $M_2(\partial n/\partial g_2)_{g_1}$ a straight line is obtained according to equation (20). This is shown in Fig. 2. From the slope of this
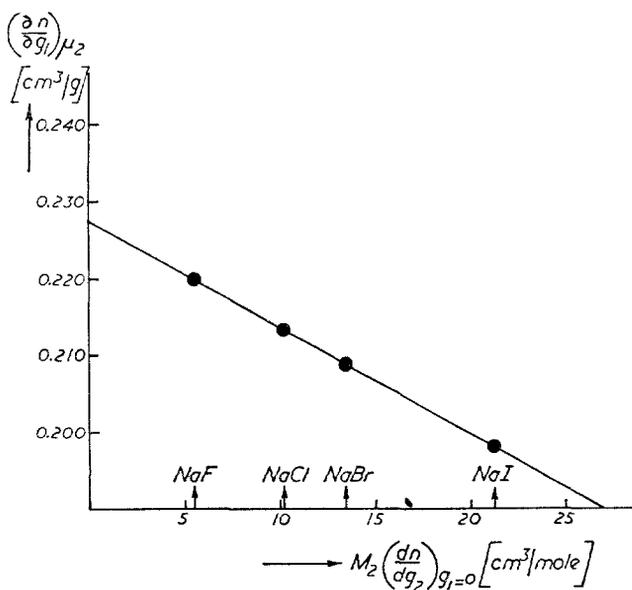
FIG. 2. Refractive index increment at constant chemical potential plotted against molar refractive index increment of supporting electrolyte.
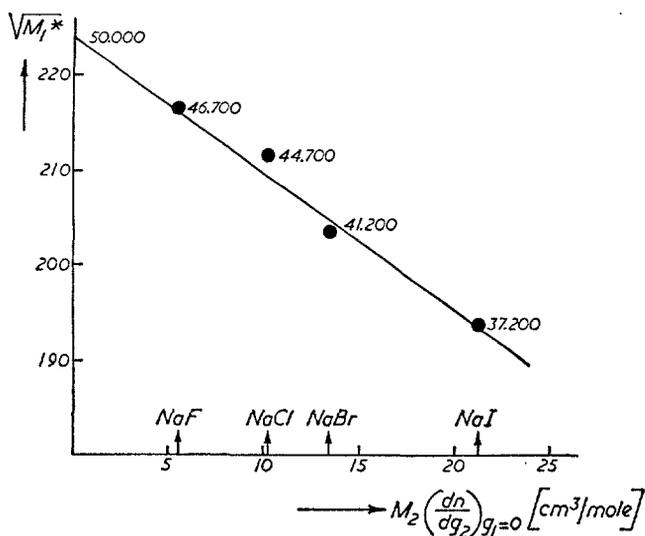
FIG. 3. Square root of the apparent molecular weight $M*_1$ plotted against molar refractive index increment of supporting electrolyte.

line a value of 0.24 mole/equiv. is found and the cut-off gives 0.227 for $(\partial n/\partial g_1)_{g_2}$.

(d) It is also possible to calculate M_1 and B without making use of the data from the Donnan equilibrium. Introducing equivalent weights in the equations (14) and (15) (cf. equation (20)), $\sqrt{M_1^*}$ or $1/\sqrt{B^*}$ for the four sodium halide solutions, taken from Table 2, may be plotted against $M_2(\partial n/\partial g_2)_{g_1}$, yielding straight lines (see Fig. 3). The cut-offs give the square roots of the true values M_1 and B, and from the slope the negative adsorption may be obtained. This procedure leads to 50,000 for the molecular weight and 0.25 mole/equiv. for the negative adsorption both in good agreement with values determined earlier. Essentially this extrapolation procedure amounts to extrapolation to a supporting electrolyte which does not influence the refractive index ($(\partial n/\partial g_2)_{g_1} = 0$).

Detergent Solutions

This last method is particularly useful for the interpretation of light scattering of detergent solutions. There all the difficulties of working with polyelectrolytes recur, but the equilibrium between monomeric soap and micelles makes it impossible to obtain true Donnan equilibria. If it is assumed that variation of the co-ions of the same valence has negligible influence on micellar size and shape, the extrapolation method illustrated in Fig. 3 can be applied to determine true micellar weights, unhampered by effects of the electric charge.

METHOD OF MEASUREMENTS

As the light scattering by detergent solutions is relatively small and as moreover detergents have a strong tendency to keep dust particles in suspension, an accurate apparatus and a good method for eliminating dust are required. We have used a light scattering apparatus built in our laboratory which combines an optical part strongly resembling that of the Sofica light scattering meter (principle described by Wippler and Scheibling, 1954) with an electrical part derived from that published by Coumou (1960). The apparatus uses a compensation method with two photomultipliers. The cells with solution are fixed in a toluene bath of constant temperature. The scattered light is intercepted by a totally reflecting prism which can be moved around the cell.

The cells are a modification of that described by Dandliker and Kraut (1956) as shown in Fig. 4. The cell is filled to the narrow neck, suspended in a swinging bucket ultracentrifuge in a liquid in which it just floats, and centrifuged at 20,000 r.p.m. (45,000 g) for $\frac{1}{2}$ to 3 hr after which all the dust is collected in the sharp part at the bottom of the cell. A Teflon stopper is

used to fix the cell in a sufficiently well defined position in the light path. In most measurements the scattering is determined at three angles, R_{45}, R_{90} and R_{135}. R_{45} and R_{135} are used to check the absence of dissymmetry. (Dissymmetry always $< 1\cdot03$). R_{90} is then used to calculate the turbidity τ.
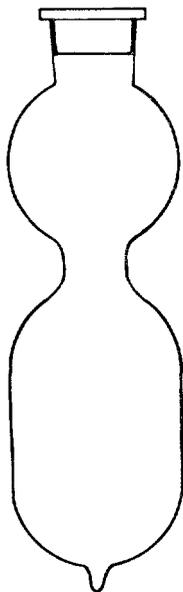
Fig. 4. Light scattering cell.

RESULTS

Measurements have been performed on highly purified sodium laurylsulfate ($C_{12}SO_4Na$) and the corresponding C_8, C_9, C_{10} and C_{11} detergents. The four sodium halides have been used as supporting electrolytes in concentrations varying between 0.01 M and 0.3 M. In this paper we shall only give the data on C_{12} for purposes of illustration.

An additional complication in the case of detergents is the presence of the monomeric soap. The turbidity of the solvent with low-molecular weight components includes the detergent up to the critical micelle concentration (c.m.c.). The colloid concentration is supposed to be equal to the detergent concentration minus the c.m.c.

Figure 5 illustrates the general course of turbidity against detergent concentration. Figures 6 and 7 show the extrapolation of the turbidity data to zero micelle concentration for $0\cdot3$ M supporting electrolyte and the plot of the extrapolated molecular weight values to a supporting electrolyte with zero refractive index increment. Figures 8, 9 and 10 are analogous with Fig. 7 but now for lower electrolyte concentrations. It is obvious that without the
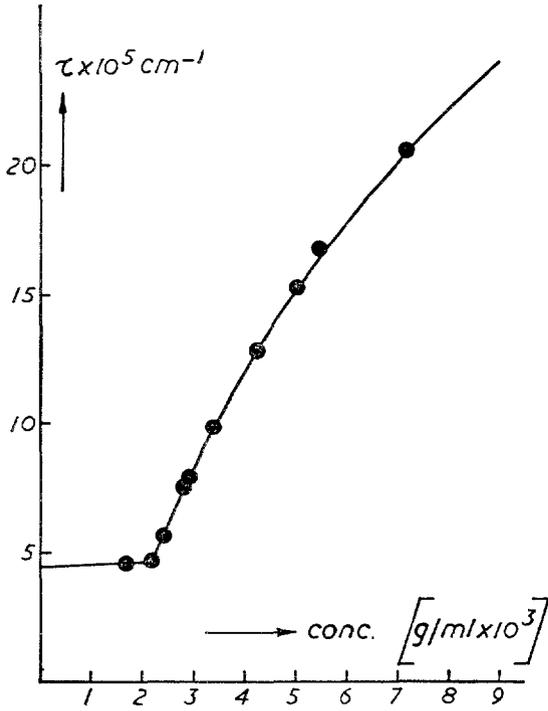
FIG. 5. Turbidity data for solutions of $C_{12}SO_4Na$ in water. Measurements at $\lambda = 436\,m\mu$.
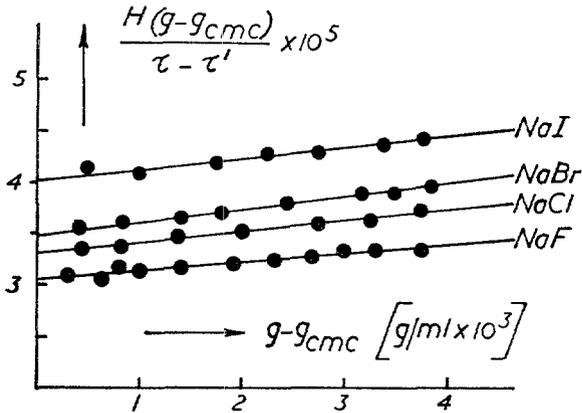
FIG. 6. Light scattering data for solutions of $C_{12}SO_4Na$ in 0.3 M Na X (X = F, Cl, Br, I). Average data from measurements at $\lambda = 436\,m\mu$ and $\lambda = 546\,m\mu$. Extrapolation to zero micellar concentration.

extrapolation the molecular weight would be underestimated by 10–40 per cent. Moreover, the slope of the lines can be used to deduce the negative adsorption. For the lowest concentrations of supporting electrolyte the concentration and the contribution to the refractive index of the monomeric detergent cannot be neglected as compared to these quantities for the inorganic salt. Therefore an average refractive index increment is used on the abscisses. This corresponds to the assumption that as far as the negative
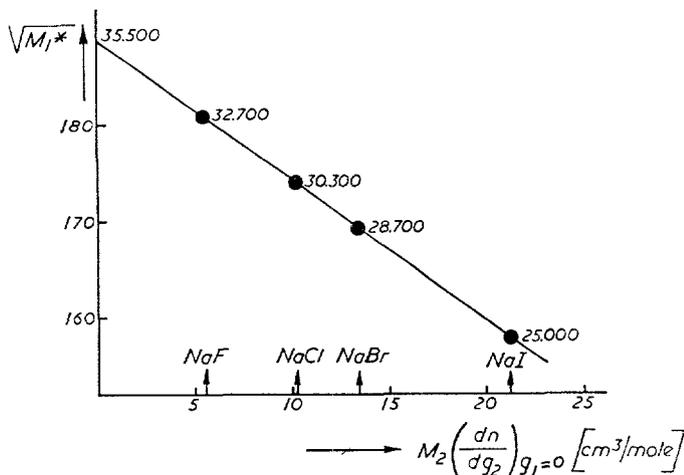
FIG. 7. Extrapolation of square root of the apparent micellar weight M_1^* to supporting electrolyte (0.3 M) with zero $M_2(\partial n/\partial g_2)_{g_1}$.
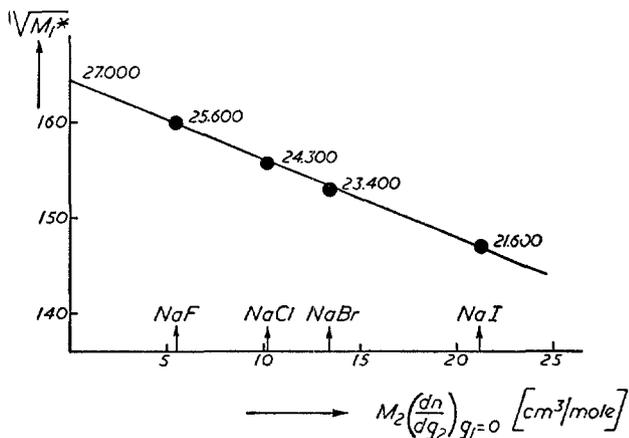
FIG. 8. Extrapolation of square root of the apparent micellar weight M_1^* to supporting electrolyte (0.1 M) with zero $M_2(\partial n/\partial g_2)_{g_1}$.

adsorption is concerned the monomeric detergent does not behave differently from the sodium halides.

Table 3 unites the values for the extrapolated micellar weight and for the negative adsorption expressed as fraction of the micellar charge compensated by the lack of anions in the double layer.

The increase in micellar weight with increasing concentration of electrolyte is in good agreement with theoretical expectations. The decrease of the double layer potential makes it easier to aggregate a larger number of mono-
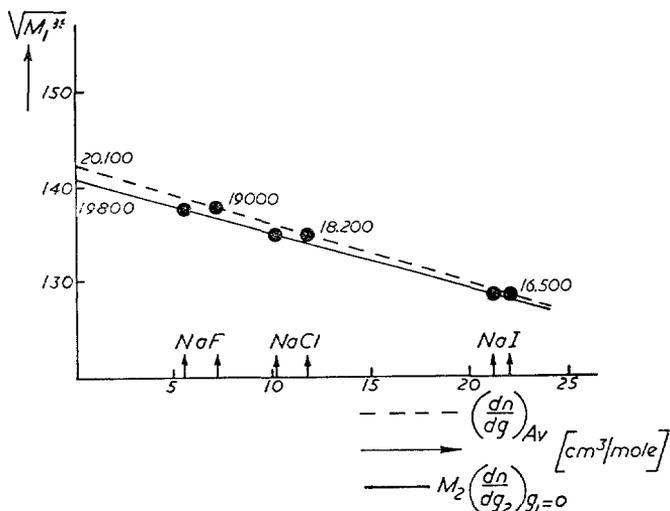
FIG. 9. Extrapolation of square root of the apparent micellar weight M_1^* against refractive increment of supporting electrolyte (———) at 0.03 M and against average refractive index increment

$$\left(\frac{dn}{dg_{Av}} = \frac{1}{g_m + g_2}\ M_{aJ}\ \frac{dn}{dg_m} + M_2 g_2 \frac{dn}{dg_2}\right)$$

of sodium halide and monomeric detergent (- - - -) (M_m, g_m).

TABLE 3. TRUE MICELLAR WEIGHT AND NEGATIVE ADSORPTION OF MICELLES OF $C_{12}SO_4Na$

Conc. of electrolyte [moles/1]	Micellar weight	Number of monomers per micelle	Neg. ads. in molecules per micelle	Neg. ads. as fraction of micellar charge
0.3	35,600	123	32	0.26
0.1	26,900	94	14.5	0.15
0.03	20,100	70	10	0.14
0.01	18,500	64	9.5	0.15

mers in one micelle. The values of the negative adsorption are reasonable, the increase with increasing electrolyte concentration agrees with the expected trend.

Further theoretical work on the interpretation of the micellar weight and negative adsorption ratio is in progress.
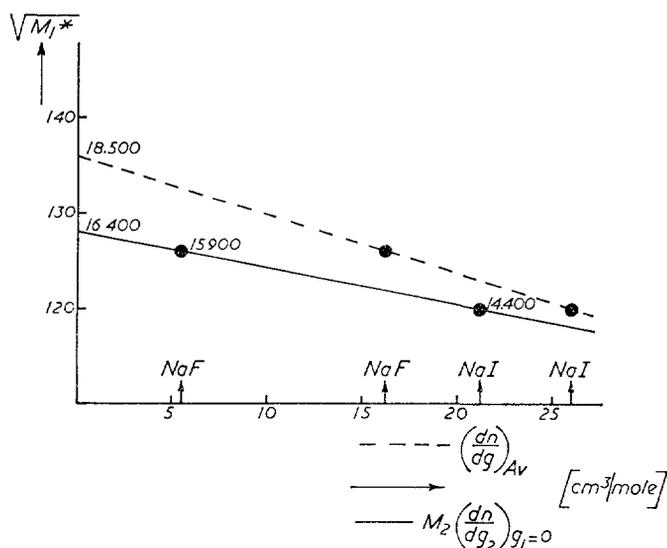
FIG. 10. Extrapolation of square root of the apparent micellar weight M_1^* against refractive increment of supporting electrolyte (——) at 0.01 M and against average refractive index increment

$$\frac{dn}{dg_{Av}} = \frac{1}{g_m + g_2}\left(M_m g_m \frac{dn}{dg_m} + M_2 g_2 \frac{dn}{dg_2}\right)$$

of sodium halide and monomeric detergent (- - - -) (M_m, g_m).

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