

SCATTERING OF LIGHT BY CHARGED COLLOIDAL PARTICLES IN SALT SOLUTIONS

A. Vrij and J. Th. G. Overbeek

van't Hoff Laboratory, University of Utrecht, the Netherlands

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ABSTRACT

In the interpretation of light scattering by colloidal electrolytes in salt solutions the interaction between the colloidal particles and the low molecular weight ions has to be taken into account. When fluctuation theory is applied for the derivation of a light-scattering equation, nonelectroneutral fluctuations may be neglected in most cases. The total light scattering can be split into three contributions, one due to density fluctuations, one due to concentration fluctuations in the low molecular weight components, and one due to the colloidal particles. In the last-named contribution the (usually negative) adsorption of the low molecular weight salts by the colloid is included. This can be taken into account in good approximation by using in the light-scattering equations the refractive index increment at constant chemical potential and not at constant concentrations of the other components of the system. This quantity can be measured directly in membrane equilibria or it can be calculated from concentration differences in a membrane equilibrium combined with the more usual refractive index increments at constant concentrations.

The theoretical treatment is confirmed by measurements of light scattering and membrane equilibria with half-neutralized polymethacrylic acid in 0.1 *M* sodium halide solutions and in a few other salts. The correction on the molecular weight varies from 10% in NaF to 25% in NaI and amounts even to 45% in 0.01 *M* $(\text{NH}_4)_6\text{M}_2\text{O}_7\text{O}_{24}$.

INTRODUCTION

In his theory of light scattering by colloidal solutions Debye (1) derived the following equation which is valid for a two-component system (colloid and solvent)

$$\frac{Hg}{\tau - \tau_0} = \frac{1}{RT} \frac{d\Pi}{dg} \quad [1]$$

Here g is the concentration of the colloid in g./cm.³, Π is the osmotic pressure against the solvent, R is the gas constant, T is the absolute temperature, and τ and τ_0 are the turbidities of solution and solvent, respectively. The factor H has the value

$$H = \frac{32\pi^3 n^2 (dn/dg)^2}{3\lambda_0^4 N_{Av.}} \quad [2]$$

where n is the refractive index of the solution, λ_0 is the wavelength in vacuum of the light used for the experiment, and N_{Av} is Avogadro's number.

With the following expression for the osmotic pressure

$$\frac{\Pi}{RT} = \frac{g}{M} + Bg^2 \quad [3]$$

Eq. [1] can be transformed into

$$\frac{Hg}{\tau - \tau_0} = \frac{1}{M} + 2Bg. \quad [4]$$

Here M is the molecular weight of the colloid and B is the second virial coefficient.

The above equations which have been derived from fluctuation theory are not wholly applicable to the case of charged colloidal particles in a salt solution. This is a three-component system where the fluctuations of colloid and salt are interdependent. Zernike (2) was the first to give a rigorous treatment of the light scattering in multicomponent systems. This treatment has been extended by Brinkman and Hermans (3), Kirkwood and Goldberg (4), Stockmayer (5), Shogenji (6), and recently by Ooi (7) and by Casassa and Eisenberg (8). In these theories suitable generalizations are derived for the quantities H (containing the refractive index increments) and $d\Pi/dg$ (related to the free energy of the system). In electrolytic solutions, however, it is hard to find accurate explicit expressions for the free energy because activity coefficients are so hard to calculate.

Mysels *et al.* (9, 10) and Prins and Hermans (11) in studying light scattering by soap micelles tried to avoid activity coefficients by ascribing an "effective charge" to the micelles and further assuming ideal behavior for the solutions. This model is not satisfactory in so far as it is not evident whether the introduction of an effective charge takes the deviations from ideality sufficiently into account. We shall return to this point in a later paper. See also reference 12, chapter 5. Recently Stigter (13) has employed statistical thermodynamic relations to express the turbidity in terms of molecular parameters, i.e., size and surface charge of the colloidal particles and the ionic strength of the solution.

The theory faces another difficulty in the long-range nature of electrostatic interactions. If the ionic strength of the solution is very small ($<10^{-3} M$), the range of the interaction between charged particles becomes comparable with the wavelength of visible light. In this case interference effects occur (14). These cannot be described by fluctuation theory in its usual form, which assumes the fluctuations in neighboring volume-elements to be independent.

In this paper light scattering by charged particles in salt solutions will be treated by fluctuation theory. Only electroneutral fluctuations will be taken into account. The charge of the colloidal particles attracts counterions

and pushes co-ions away, thus causing a negative adsorption of added salts. This negative adsorption fluctuates as a whole with the particles, so that one may say that the particle plus its complete surroundings is the scattering unit. The *amount* of negative adsorption can be determined exactly in a membrane equilibrium (Donnan equilibrium) between the colloid solution and a solution containing only its small molecular weight components.

FLUCTUATION THEORY

The scattering solution, which may be a multicomponent system, is divided into volume elements ΔV . The refractive index in such a volume element will fluctuate around a mean value owing to the Brownian motion of the particles.

Fluctuation theory may be applied if the following conditions are satisfied:

a. In order to keep phase differences negligible, the volume-elements ΔV should be small with respect to the wavelength of the light used.

b. However, the volume-elements should be large enough to make concentration fluctuations in a given volume-element independent of those in neighboring volume-elements (15).

If both these conditions are satisfied, the volume-elements may be considered as radiating dipoles the amplitudes of which fluctuate independently. Consequently the total scattering of the solution is equal to the sum of the contributions of all volume-elements. It may be written as follows (2, 3):

$$\tau = \frac{32\pi^3 \bar{n}^2 V \overline{(\Delta n)^2}}{3\lambda_0^4} \quad [5]$$

Here $\Delta n = n - \bar{n}$; n and \bar{n} are the refractive index and the mean refractive index, respectively, in a volume V ; τ is the turbidity; λ_0 is the wavelength *in vacuo*.

We consider a scattering volume V , with a volume element ΔV in the shape of a slice with thickness d (Fig. 1).

The maximum phase difference of light rays (with wavelength λ_m in the medium) scattered under an angle θ by the volume element is equal to $2d(\sin(\theta/2))/\lambda_m$. Hence to satisfy condition (*a*) this quantity should be small with respect to unity.

In order to satisfy condition (*b*) the size of the particles and the range of the intermolecular forces (say r_0) should be small with respect to the thickness d of the volume element ($r_0 \ll d$). For short-range forces and visible light both conditions can be satisfied for all scattering angles. For long-range forces, however, it is necessary to measure the scattering under such a small angle that $2r_0 \sin(\theta/2)/\lambda_m$ be small with respect to unity. In order to find the scattering at larger angles, the correlations between different volume

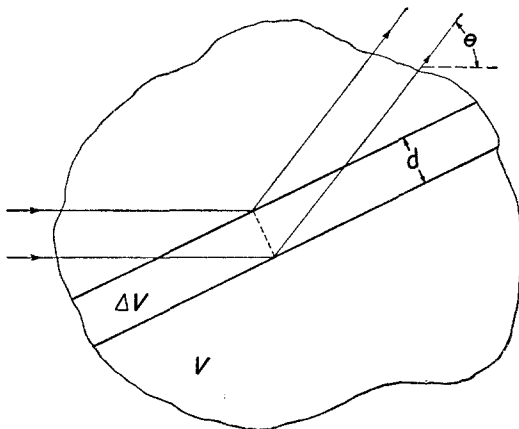


Fig. 1. Light scattered by the slice ΔV has a maximum phase difference $(2d/\lambda_m)\sin(\theta/2)$.

elements have to be taken into account, but extrapolation to a scattering angle $\theta = 0$ restores the validity of Eq. [5].

CHARGED PARTICLES

In systems containing charged particles such as proteins, polyelectrolytes, and simple electrolytes, the range of the electrostatic forces is given by the thickness, $1/K$, of the Debye-Hückel ionic atmosphere, where

$$\frac{1}{K} = \sqrt{\frac{DkT}{4\pi \sum_i e_i^2 c_i}}, \quad [6]$$

and D is the dielectric constant of the medium, k the Boltzmann constant, e_i the ionic charge, and c_i the average number of ions of type i per unit volume. Beyond a distance of a few times $1/K$ from a charged particle systematic concentration differences are negligible. Hermans (15) has shown that in volume-elements whose linear dimensions are larger than $1/K$, nonelectroneutral fluctuations may be neglected as compared to neutral fluctuations. Consequently, the fluctuation theory may be applied to systems containing charge particles if

$$\frac{2 \sin \theta/2}{K\lambda_m} \ll 1. \quad [7]$$

In order to keep deviations below 1% the left-hand side of expression [7] should be smaller than 0.05. See reference 15. For visible light this condition obtains for all angles, if $K > 1/(100 \text{ \AA.})$ or in aqueous solutions when the ionic strength is more than 10^{-3} molar. We shall restrict our considerations to cases where Eq. [7] is satisfied.

DERIVATION OF A LIGHT-SCATTERING EQUATION FOR A CHARGED COLLOID
IN A SALT SOLUTION

In a system of $m + 1$ components ($i = 0, 1, 2 \dots m$) the mean square of the fluctuation in the refractive index $(\overline{\Delta n})^2$ (see Eq. [5]) can be written:

$$\overline{\Delta n^2} = \sum_{i,k=0}^m n_i n_k \overline{\Delta N_i \Delta N_k} = kT \sum_{i,k=0}^m n_i n_k (\partial \bar{N}_i / \partial \mu_k)_{\mu V T}, \quad [8]$$

where $n_i = (\partial n / \partial N_i)_{TVN}$; N_i is the number of particles of type i in volume V ; $\Delta N_i = N_i - \bar{N}_i$; μ_k is the chemical potential of component k . The indices N, μ mean that all N_j, μ_j , except N_i, μ_i are kept constant in the differentiation with respect to N_i or μ_i , respectively. In the following discussion the index T will be omitted for the sake of simplicity.

The first equality in Eq. [8] is self-evident. The second one is based on the relation

$$\overline{\Delta N_i \Delta N_k} = kT (\partial \bar{N}_i / \partial \mu_k)_{\mu V} = kT (\partial \bar{N}_k / \partial \mu_i)_{\mu V}, \quad [9]$$

which was obtained by Zernike (2) using Gibbs' grand canonical ensemble.

Writing

$$\Xi = \sum_{l, \underline{N}} \exp \frac{N \cdot \underline{\mu} - E_l}{kT} \quad [10]$$

for the sum of states in the grand ensemble (16), where l indicates the different energy levels of the system, \underline{N} the different sets of $N_0, N_1 \dots N_m$, and $N \cdot \underline{\mu} = \sum_{i=0}^m N_i \mu_i$, we find the average value of N_j from

$$\bar{N}_j \Xi = \sum_{l, \underline{N}} N_j \exp \frac{N \cdot \underline{\mu} - E_l}{kT}. \quad [11]$$

Differentiation with respect to μ_k then leads to the desired relation [9].

$$\frac{\partial \bar{N}_j}{\partial \mu_k} \Xi + \bar{N}_j \sum_{l, \underline{N}} \frac{N_k}{kT} \exp \frac{N \cdot \underline{\mu} - E_l}{kT} = \sum_{l, \underline{N}} \frac{N_j N_k}{kT} \exp \frac{N \cdot \underline{\mu} - E_l}{kT}$$

or

$$\frac{\partial \bar{N}_j}{\partial \mu_k} = - \frac{\bar{N}_j \bar{N}_k}{kT} + \frac{\overline{N_j N_k}}{kT} = \frac{\overline{(N_j - \bar{N}_j)(N_k - \bar{N}_k)}}{kT} = \frac{\overline{\Delta N_j \Delta N_k}}{kT}.$$

Before inserting Eq. [8] into the light-scattering Eq. [5] it is desirable to apply some transformation. In the first place the condition $V = \text{constant}$ will be eliminated from the differential quotients $n_i = (\partial n / \partial N_i)_{VN}$. Further, the total light scattering will be split into three contributions, one containing the density fluctuations, mainly from the solvent (component 0), one containing the concentration fluctuations of the colloid with an equivalent amount of counterions (component 1) including the contribu-

tion from the positive or negative adsorption of the low molecular weight salts and other solutes (components $2 \cdots m$) to the colloid, and one derived from the concentration fluctuations of the remainder of the components $2 \cdots m$. Ooi (7) has given such a derivation for a neutral polymer in a mixture of solvents. Casassa and Eisenberg (8) developed the theory for a polyelectrolyte with salt. Independently an analogous derivation was given by one of us (12) for the ionic case.

In Appendix I Eq. [12] is derived from Eq. [5] and Eq. [8].

$$\frac{\tau}{A} = [V^2 n_V^2 - \phi^2] \kappa + \frac{\left[\sum_{i=1}^m \gamma_i \left(\frac{\partial c_i}{\partial c_1} \right)_{\mu_s} \right]^2}{(\partial \Pi / \partial c_1)_{\mu_s}} c_1 + \sum_{i,k=2}^m \gamma_i \gamma_k (\partial c_i / \partial \mu_k)_{\mu_s', c_1}. \quad [12]$$

In this equation

$$A = 32\pi^3 \bar{n}^2 kT / 3\lambda_0^4; \quad [13]$$

$$n_V = (\partial n / \partial V)_N; \quad [14]$$

$$\phi = \sum_{i=1}^m \gamma_i c_i; \quad [15]$$

$$\gamma_i = (\partial n / \partial c_i)_{P,c}; \quad [16]$$

$$c_i = \bar{N}_i / V; \quad [17]$$

$$\kappa = -(\partial V / V \partial P)_N; \quad [18]$$

P = pressure;

Π = osmotic (Donnan) pressure difference between the solution and a solution in equilibrium with it but containing only the low molecular weight components.

The index $\mu_s, (\mu_s')$ means that the chemical potentials of all the solutes (all solutes except the one used in the differentiation) are kept constant.

The first term of Eq. [12] is due to density fluctuations, the second term to the colloid including the contribution from the positive or negative adsorption of the noncolloidal solutes, and the third one to the concentration fluctuations of the remainder of the noncolloidal solutes. For a salt solution without colloid (components $0, 2, \cdots m$) one obtains

$$\frac{\tau^*}{A} = [V n_V^{*2} - \phi^{*2}] \kappa^* + \sum_{i,k=2}^m \gamma_i^* \gamma_k^* (\partial c_i / \partial \mu_k)_{\mu_s', c_1=0} \quad [19]$$

We have labeled the variables here with an asterisk.

It is shown by a numerical argument in Appendix II that τ^*/A can be put equal to the corresponding unstarred terms of Eq. [12] in very good approximation:

$$\frac{\tau^*}{A} \simeq [V n_V^2 - \phi^2] \kappa + \sum_{i,k=2}^m \gamma_i \gamma_k (\partial c_i / \partial \mu_k)_{\mu_s', c_1}$$

and consequently

$$\frac{\tau - \tau^*}{A} = \frac{\left[\sum_{i=1}^m \gamma_i (\partial c_i / \partial c_1)_{\mu_s} \right]^2}{(\partial \Pi / \partial c_1)_{\mu_s}} c_1, \quad [20]$$

where τ^* is the turbidity of the salt solution without colloid in Donnan equilibrium with the solution of turbidity τ .

The term $\Sigma \gamma_i (\partial c_i / \partial c_1)_{\mu_s}$ can be treated in two different ways.

a. The refractive index increments $\gamma_i = (\partial n / \partial c_i)_{Pc}$ can be measured directly at normal pressure, and $(\partial c_i / \partial c_1)_{\mu_s}$, being the adsorption of component i on the colloid, can be determined in a Donnan membrane equilibrium with an outside solution with chemical potentials μ_s and an inside solution with colloid concentration c_1 (or it may be calculated in special cases).

The determination of $(\partial c_i / \partial c_1)_{\mu_s}$ should strictly be carried out at the pressure of the Donnan cell, but the relative compressibility correction is of the order of $\kappa c (\partial \Pi / \partial c_1)_{\mu_s} / (\partial c_i / \partial c_1)_{\mu_s} < 1 / M_{\text{colloid}}$ and is thus completely negligible.

b. It is also possible to determine the sum $\Sigma \gamma_i (\partial c_i / \partial c_1)_{\mu_s}$ directly by allowing the Donnan equilibrium to be established between two solutions with a difference in concentration (Δc_1) of the colloid, separating the solutions and measuring the difference in refractive index (Δn). Then $\Delta n / \Delta c_1$ is again with a relative error of the order $\kappa c (\partial \Pi / \partial c_1) / (\partial c_i / \partial c_1)$ equal to the above-mentioned sum.

In Ooi's analysis (7) the term $\Sigma \gamma_i (\partial c_i / \partial c_1)_{\mu_s}$ is replaced by $(\partial n / \partial c_1)_{\mu_s}$, the value of τ^* being also slightly changed. In $(\partial n / \partial c_1)_{\mu_s}$ the increments of the refractive index and of the concentration c_1 should both be measured at the Donnan pressure. The difference, however, with $\Delta n / \Delta c_1$ as defined above and with $\Sigma \gamma_i (\partial c_i / \partial c_1)_{\mu_s}$ is again of the order of $1 / M_{\text{colloid}}$.

When concentrations by weight are introduced, $g_i = c_i M_i / N_{Av}$, where M_i is the molecular weight of component i , Eq. [20] can be transformed into

$$\frac{H' g_1}{\tau - \tau^*} = \frac{1}{RT} \left(\frac{\partial \Pi}{\partial g_1} \right)_{\mu_s}, \quad [21]$$

where

$$H' = \frac{32\pi^3 \bar{n}^2}{3\lambda_0^4 N_{Av}} \left(\frac{\partial n}{\partial g_1} \right)_{\text{Donnan}}^2 \quad [22]$$

and $(\partial n / \partial g_1)_{\text{Donnan}}$ is the refractive index increment measured between the two solutions of a Donnan equilibrium, but brought to the same pressure.

The Donnan pressure Π may be expanded into a power series in g_1 (17, 18)

$$\Pi / RT = g_1 / M_1 + B(\mu_s) g_1^2 + D(\mu_s) g_1^3 + \dots \quad [23]$$

Introducing this expression into Eq. [21] leads to

$$\frac{H'g_1}{\tau - \tau^*} = \frac{1}{M_1} + 2B(\mu_s)g_1 + \text{etc.} \quad [24]$$

an expression differing only from the traditional expression [4] in that τ^* now represents the scattering by the mixture of solvent(s) and low molecular weight salts and in that H' contains a refractive index increment at constant chemical potential rather than at constant concentration.

In an actual dilution series the concentration of the salts rather than their chemical potential will be kept constant. This implies that for each concentration of the colloid the chemical potentials μ_s will have slightly different values. This affects H' , τ^* , and B . The influence on H' is due to higher order effects such as $(\partial^2 n / \partial g_i \partial g_j)$ and $(\partial^2 g_i / \partial g_1^2)$ and may be neglected.

It has been mentioned in Appendix II that the influence on τ^* is small compared to the difference between τ^* and τ^{0*} and may also be neglected. The second virial coefficient finally may be written

$$B(\mu_s) = B(\mu_s^0) + \frac{\partial B}{\partial \mu_s} \left(\frac{\partial \mu_s}{\partial g_1} \right)_g g_1 + \dots \quad [25]$$

and the correction term therefore would affect only higher terms than the ones written in Eq. [24].

TRUE AND APPARENT MOLECULAR WEIGHT AND SECOND VIRIAL COEFFICIENT

The use of Eq. [24] allows the calculation of the true molecular weight M_1 and the true second virial coefficient B from turbidity measurements, provided $(\partial n / \partial g_1)$ has been determined with a correct procedure, i.e., using a membrane equilibrium. If, however, a refractive index increment at constant concentrations $(\partial n / \partial g_1)_{g_2 \dots g_m}$ is substituted in expression [22] for H' , then an incorrect or apparent molecular weight M_1^* and second virial coefficient B^* are found. If only one low molecular weight salt is present (component 2), the relation between M_1 and M_1^* is

$$M_1^* = M_1 \left[1 + \frac{(\partial n / \partial g_2)_g}{(\partial n / \partial g_1)_g} \left(\frac{\partial g_2}{\partial g_1} \right)_{\mu_2} \right]^2 \quad [26a]$$

and the relation between B and B^* is

$$B^* = B \left[1 + \frac{(\partial n / \partial g_2)_g}{(\partial n / \partial g_1)_g} \left(\frac{\partial g_2}{\partial g_1} \right)_{\mu_2} \right]^2. \quad [26b]$$

Relations equivalent to Eq. [26a] were already used by Stockmayer (5) and by Ooi (7) in the discussion of the adsorption from a mixed solvent to an uncharged polymer as measured by Ewart *et al.* (19). More recently

Strauss and Wineman (20) used an equation equivalent to Eq. [24] for the determination of the molecular weight of polyphosphates. They determined a quantity analogous to $(\partial g_2/\partial g_1)_{\mu_2}$ from membrane equilibria.

THE NEGATIVE ADSORPTION OF SALT

The most obvious contribution to $(\partial g_2/\partial g_1)_{\mu_2}$ is caused by the electrical double layer. If we neglect any specific effects, the double layer is always a seat of negative adsorption of the supporting electrolytes. Assuming for simplicity this to be NaCl, the concentrations of the ions in the double layer are given by

$$\begin{aligned} c_{Na} &= c_2 \exp(-e\psi/kT); \\ c_{Cl} &= c_2 \exp(+e\psi/kT). \end{aligned} \quad [27]$$

Here e is the elementary charge, and ψ is the potential in the double layer. It has been pointed out repeatedly (for example, Overbeek (21)) that according to Eq. [27] the excess of counterions and the deficit of co-ions are equal when the potential is low, but that at increasing potential the excess of counterions rises much faster than the deficit of co-ions. See Fig. 2.

The difference between the amounts of counterions and co-ions just compensates the particle charge ze . The negative adsorption of salt is equal to the deficit of co-ions and thus equal to αz molecules per particle, where $\alpha = 1/2$ for low potentials and $\alpha < 1/2$ for high potentials. Stigter (22), for example, has calculated α for spherical micelles of sodium-laurylsulfate with a charge of about 100 and has found $\alpha \sim 0.085$.

We may thus write

$$\left(\frac{\partial g_2}{\partial g_1}\right)_{\mu_2} = \frac{M_2}{M_1} \left(\frac{\partial c_2}{\partial c_1}\right)_{\mu_2} = -\frac{M_2 z \alpha}{M_1} \quad [28]$$

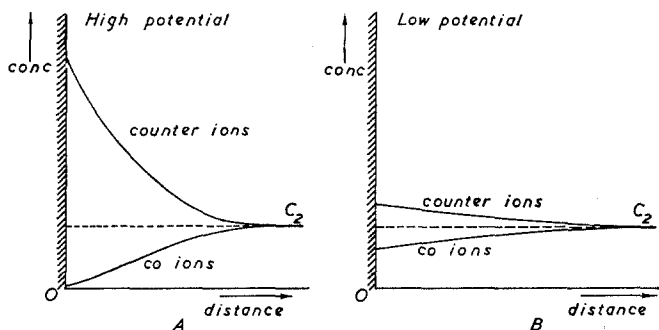


FIG. 2. Illustrating the distribution of ions in double layers. A for high potentials; B for low potentials.

and

$$M_1^* = M_1 \left(1 - \alpha z \frac{M_2 (\partial n / \partial g_2)_g}{M_1 (\partial n / \partial g_1)_g} \right)^2 \quad [29]$$

Mysels and co-worker (9, 10) have treated the light scattering by micelles of sodiumlaurylsulfate assuming incomplete dissociation (effective charge $z_{eff} \cdot e < ze$) combined with ideal behavior. They obtain an equation which can be written in a first approximation

$$M_1^* = M_1 \left(1 - \frac{z_{eff}}{2} \frac{M_2 (\partial n / \partial g_2)_g}{M_1 (\partial n / \partial g_1)_g} \right)^2 \quad [30]$$

Their z_{eff} is therefore equal to $2\alpha z$, twice the negative adsorption according to the above treatment. They find $z_{eff} \approx 15$, nearly identical with $2\alpha z = 17$, which follows from Stigter's work.

EXPERIMENTS

The theory developed above has been tested with solutions of polymethacrylic acid (PMA) in aqueous HCl and in various salt solutions. In HCl no double layer effects are to be expected, because the polymer is uncharged. In salt solutions, the polymer was half neutralized by addition of NaOH, and charge effects are pronounced. As the structure of the polymer coil is mainly determined by the concentration and valence of the cations, while the optical effects are just as much determined by the anions, we have directed our attention in particular to variation of the anions.

PREPARATION OF THE POLYMER

PMA was prepared according to the method of Arnold and Overbeek (23) with H_2O_2 and Fe^{3+} -ions as the catalyst (50 g. methacrylic acid, 67 ml. 0.03 M H_2O_2 , 70 ml. 0.03 M $FeSO_4$, and 500 ml. H_2O). The PMA thus obtained has not been fractionated sharply; care has been taken only to get rid of the highest and lowest molecular weights by precipitation with HCl from aqueous solutions. To remove the iron the PMA was dissolved in an NaOH solution and filtered. Colloidal $Fe(OH)_3$, however, is still present after this procedure. Upon addition of acetone the $Fe(OH)_3$ precipitates together with a small amount of polymer and then the supernatant polymer solution can be decanted. The alkaline-polymer solution was then neutralized with HCl and dialyzed against distilled H_2O ; subsequently the solution was electro-dialyzed against conductivity water during 5 days. The solution obtained in this way was diluted to about 2% as determined by titration with NaOH. It still contained a trace (less than 0.005% calculated on the polymer) of iron.

REFRACTIVE INDEX INCREMENT

A known weight of the stock solution of PMA was half neutralized by NaOH and after adding a known weight of salt, was diluted with distilled water to 50 ml. The refractive index increment determined was sufficiently independent of the wavelength to allow determination with white light in a

TABLE I
Refractive Index Increments of Salt and of PMA at 20°C.

Solvent	$M_2 \left(\frac{\partial n}{\partial g_2} \right)_{g_1=0}$ (ml./mole)	$\left(\frac{\partial n}{\partial g_1} \right)_{g_2}$ (ml./g.)	$\left(\frac{\partial n}{\partial g_1} \right)_{\mu_2}$ (ml./g.)
0.045 <i>M</i> HCl	—	0.156	0.162
0.1 <i>M</i> NaF	5.5	0.229	0.219
0.1 <i>M</i> NaCl	10.2	—	0.213
0.1 <i>M</i> NaBr	13.4	0.234	0.209
0.1 <i>M</i> NaI	21.2	—	0.197
0.1 <i>M</i> Na ₂ SO ₄	21.3	—	0.210
0.01 <i>M</i> (NH ₄) ₆ Mo ₇ O ₂₄	—	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.

Rayleigh interferometer (fabricated by Zeiss). It was determined for constant salt concentration (usually 0.1 *M*) and various PMA concentrations (maximum 0.15%). The solutions were then dialyzed against the same salt concentration. After about 24 hours equilibrium was established; the polymer concentration had not changed materially. The refractive index increment (now at constant chemical potential) was again determined. The results are given in Table I.

SCATTERING OF LIGHT

Scattering of light at angles of 45, 90, and 135 degrees with the incident beam was measured with a Brice-Phoenix apparatus at 546 m μ . For each salt concentration a series of polymer concentrations (half neutralized with NaOH) were investigated. With the HCl solution dissymmetry was nearly absent ($z = I_{45}/I_{135} = 1.02$; $P_{90}^{-1} = 1.014$; for notation see Doty and Steiner (24)); in the salt solutions it was somewhat higher (average $z = 1.1$; $P_{90}^{-1} = 1.08$). The turbidity τ used in our equations has been calculated from the light scattered at 90° by the equation

$$\tau = \frac{I_{90^\circ} r^2}{I_{\text{prim.}}} P_{90}^{-1} \frac{16\pi}{3}, \quad [31]$$

where r is the distance from the primary beam.

In Fig. 3 the values of $Hg_1/(\tau - \tau^*)$ have been plotted against g_1 , the PMA concentration. The refractive index increment in H was taken at constant salt concentration. So the lines extrapolate to $1/M^*$ rather than to $1/M_1$ and have a slope B^* rather than B . In all cases, except for HCl solutions, the average value 0.230 has been used for $(\partial n/\partial g_1)_{g_2}$.

The line for HCl is nearly horizontal, indicating a very small interaction between polymer particles. In salt solutions where the polymer is charged,

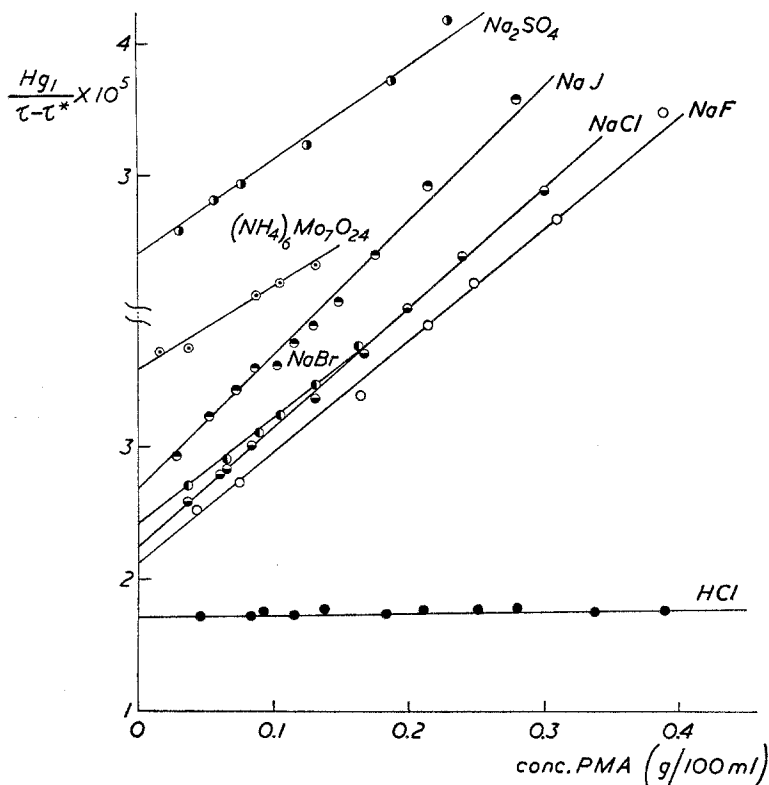


FIG. 3. $Hg_1/(\tau - \tau^*)$ plotted against concentration PMA. The data for Na_2SO_4 have been shifted upwards for clarity.

TABLE II
Apparent and True Molecular Weight and Second Virial Coefficient of PMA

Solvent	$M_1^* \times 10^{-3}$	$M_1 \times 10^{-3}$	$B^* \times 10^8$ (ml./g.)	$B \times 10^8$ (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 Na_2SO_4	41.5	49.8	3.42	2.85
0.01 M $(NH_4)_6Mo_7O_{24}$	28	52	2.95	1.59

the slope is pronounced, indicating strong repulsion between the particles. The cut-offs on the ordinate correspond to $1/M_1^*$ (Eq. [26a]) and the slopes to B^* (Eq. [26b]). They are different for each of the salts. If the correction factor $[1 + (\partial g_2/\partial g_1)_{\mu_2}(\partial n/\partial g_2)_o/(\partial n/\partial g_1)_o]^2$ is applied, the true

molecular weight M_1 found from the different salt solutions appears to be 51.000 ± 1000 . The second virial coefficients, B , for the different halides are nearly identical, indicating that the interactions between pairs are also very similar. See Table II.

NEGATIVE ADSORPTION AND EXTRAPOLATION PROCEDURE FOR THE MOLECULAR WEIGHT

The difference between the refractive index increment at constant concentration and at constant chemical potential of the supporting electrolyte is directly connected with the (negative) adsorption of the salt to the polymer.

The salt adsorption in grams per gram of polymer, $(\partial g_2/\partial g_1)_{\mu_2}$ or in moles per equivalent weight of polymer $\partial(g_2/M_2)/\partial(g_1/E)_{\mu_2}$ can be determined from the following equation

$$\begin{aligned} (\partial n/\partial g_1)_{\mu_2} &= (\partial n/\partial g_1)_g + (\partial n/\partial g_2)_g (\partial g_2/\partial g_1)_{\mu_2} \\ &= (\partial n/\partial g_1)_g + \left(\frac{\partial n}{\partial g_2}\right)_g \frac{M_2}{E} \frac{\partial(g_2/M_2)}{\partial(g_1/E)}, \end{aligned} \quad [32]$$

where E is the equivalent weight of the polymer (half neutralized!, $E = 172$) and M_2 is the formula weight of the salt. Some values of the negative adsorption can be calculated with the help of Table I, but they are not very accurate. Nevertheless it is obvious that all the salts are negatively adsorbed, $((\partial n/\partial g_1)_{\mu_2} < (\partial n/\partial g_1)_g)$, in agreement with simple electrostatic theory. The slight positive adsorption of HCl must be due to a more specific effect.

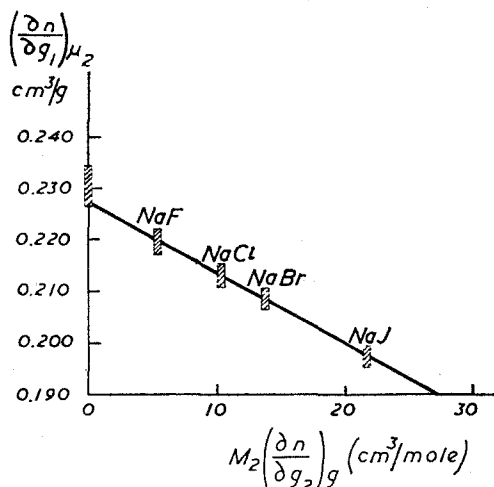


FIG. 4. Refractive index increment at constant chemical potential plotted against molar refractive index increment of salt.

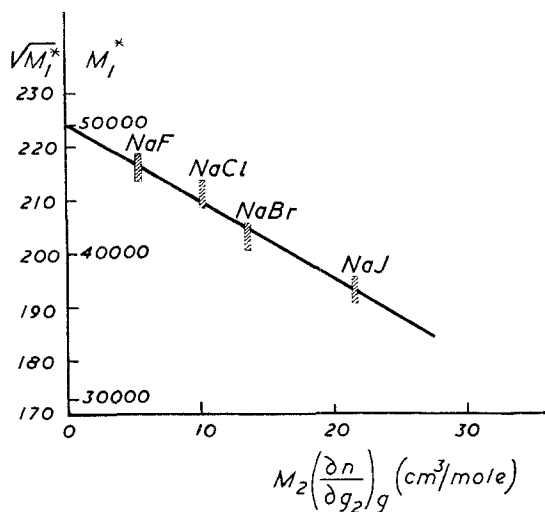


FIG. 5. Square root of the apparent molecular weight M_1^* plotted against molar refractive index increment of salt.

A more accurate value for the negative adsorption can be obtained on the assumption that it has the same value for the four halides. Then, if $(\partial n/\partial g_1)_{\mu_2}$ is plotted against $M_2(\partial n/\partial g_2)_g$, the slope of the straight line obtained gives the negative adsorption and the cut-off on the axis the value of $(\partial n/\partial g_1)_{g_2}$ as follows from Eq. [32]. From the plot in Fig. 4 the negative adsorption of the halides appears to be 0.24 mole/equivalent of polymer.

Similar use can be made of Eq. [26a]. By plotting the square root of the apparent molecular weight ($\sqrt{M^*}$) against $M_2(\partial n/\partial g_2)_g$ (Fig. 5) a straight line is obtained.

From the cut-off the true molecular weight is found ($M = 50000$) and the slope gives the negative adsorption $(\partial(g_2/M_2)/\partial(g_1/E))_{\mu_2} = 0.25$ mole/equivalent), both in very good agreement with the values determined earlier. An attractive feature of this method is that it foregoes the use of the membrane equilibrium and the separate determination of the negative adsorption. It allows determination of the molecular weight and the negative adsorption from conventional light-scattering and refractive index increment measurements only.

APPENDIX I

DERIVATION OF THE LIGHT-SCATTERING Eq. [12]

For the conversion of Eq. [8]

$$\frac{\overline{\Delta n^2}}{kT} = \sum_{i,k=0}^m (\partial n/\partial N_i)_{VTN} (\partial n/\partial N_k)_{VTN} (\partial N_k/\partial \mu_i)_{VT\mu}, \quad [8]$$

auxiliary equations for $(\partial n/\partial N_i)_{VTN}$ are first derived, in which the concentrations c_i ($i = 1 \cdots m$) and P are considered as the independent variables instead of N_i ($i = 0 \cdots m$) and V :

$$\begin{aligned} \left(\frac{\partial n}{\partial N_i}\right)_{VN} &= \left(\frac{\partial n}{\partial N_i}\right)_{P,N} + \left(\frac{\partial n}{\partial V}\right)_N \left(\frac{\partial V}{\partial P}\right)_N \left(\frac{\partial P}{\partial N_i}\right)_{V,N} \\ &= \left(\frac{\partial n}{\partial N_i}\right)_{P,N} - \left(\frac{\partial n}{\partial V}\right)_N \left(\frac{\partial V}{\partial N_i}\right)_{P,N} = \left(\frac{\partial n}{\partial N_i}\right)_{P,N} - n_V V_i \\ &= \sum_{k=1}^m \left(\frac{\partial n}{\partial c_k}\right)_{P,c} \left(\frac{\partial c_k}{\partial N_i}\right)_{P,N} - n_V V_i. \end{aligned}$$

With $c_k = N_k/V$ this is transformed into

$$\begin{aligned} \left(\frac{\partial n}{\partial N_i}\right)_{VN} &= \left(\frac{\partial n}{\partial c_i}\right)_{P,c} \frac{1}{V} - \sum_{k=1}^m \left(\frac{\partial n}{\partial c_k}\right)_{P,c} \frac{c_k}{V} \left(\frac{\partial V}{\partial N_i}\right)_{P,N} - n_V V_i \\ &= [\gamma_i - V_i(n_V V + \phi)]/V. \end{aligned} \quad [A1]$$

It should be remembered that γ_i does not exist for $i = 0$. Inserting the expressions [A1] into Eq. [8] leads to

$$\begin{aligned} \frac{\Delta n^2}{kT} &= \frac{1}{V^2} \sum_{i,k=1}^m \gamma_i \gamma_k (\partial N_k/\partial \mu_i)_{V,\mu} \\ &\quad - \frac{2(n_V V + \phi)}{V^2} \sum_{i=1}^m \gamma_i V_k (\partial N_k/\partial \mu_i)_{V,\mu} \\ &\quad + \frac{(n_V V + \phi)^2}{V^2} \sum_{i,k=0}^m V_i V_k \left(\frac{\partial N_k}{\partial \mu_i}\right)_{V,\mu}. \end{aligned} \quad [A2]$$

Using the Gibbs-Duhem relation and differentiating with respect to N_k at constant V and $N_0 \cdots N_{k-1}, N_{k+1} \cdots N_m$ we obtain

$$V(\partial P/\partial N_k)_{VN} = \sum_{l=0}^m N_l (\partial \mu_l/\partial N_k)_{V,N}. \quad [A3]$$

Substituting

$$(\partial P/\partial N_k)_{V,N} (\partial N_k/\partial V)_{P,N} (\partial V/\partial P)_N = -1$$

and

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_N$$

we find

$$V_k = \kappa \sum_{l=0}^m N_l (\partial \mu_l/\partial N_k)_{V,N}. \quad [A4]$$

Further,

$$\sum_{k=0}^m (\partial\mu_l/\partial N_k)_{V,N} (\partial N_k/\partial\mu_i)_{\mu,V} = (\partial\mu_l/\partial\mu_i)_{V,\mu} = \delta_{il},$$

where $\delta_{il} = 0$ if $i \neq l$ and $\delta_{il} = 1$ if $i = l$. Inserting [A4] into [A2] and carrying out the summation over k leads to

$$\begin{aligned} \frac{V^2 \overline{\Delta n^2}}{kT} = & \sum_{i,k=1}^m \gamma_i \gamma_k (\partial N_k/\partial\mu_i)_{V,\mu} - 2(n_V V + \phi)\kappa \sum_{i=1}^m \gamma_i N_i \delta_{il} \\ & + (n_V V + \phi)^2 \kappa \sum_{i=0}^m V_i N_i \delta_{il}. \end{aligned} \tag{A5}$$

With $\sum_{i=1}^m \gamma_i N_i = V\phi$ and $\sum_{i=0}^m V_i N_i = V$ this expression reduces to

$$\frac{V \overline{\Delta n^2}}{kT} = (V^2 n_V^2 - \phi^2)\kappa + \frac{1}{V} \sum_{i,k=1}^m \gamma_i \gamma_k (\partial N_k/\partial\mu_i)_{V,\mu}. \tag{A6}$$

It is convenient to transform the differentiation with $\mu_1 = \text{constant}$ in Eq. [A6] into one with $N_1 = \text{constant}$ but keeping to $\mu = \text{constant}$ for the other components. This will be indicated by the suffix μ_s . We find

$$\begin{aligned} \text{for } i, k \neq 1 \quad (\partial N_k/\partial\mu_i)_{V,\mu} = & (\partial N_k/\partial\mu_i)_{V,\mu_s, N_1} \\ & + (\partial N_k/\partial N_1)_{V,\mu_s} (\partial N_1/\partial\mu_i)_{V,\mu} \end{aligned} \tag{A7}$$

$$\begin{aligned} \text{for } i = 1 \quad \text{or} \quad k = 1 \quad (\partial N_k/\partial\mu_i)_{V,\mu} \\ = & (\partial N_k/\partial N_1)_{V,\mu_s} (\partial N_1/\partial\mu_i)_{V,\mu}. \end{aligned}$$

Applying Eq. [9] leads to

$$(\partial N_1/\partial\mu_i)_{V,\mu} = (\partial N_i/\partial\mu_1)_{V,\mu_s} = \frac{(\partial N_i/\partial N_1)_{V,\mu_s}}{(\partial\mu_1/\partial N_1)_{V,\mu_s}}. \tag{A8}$$

From the Gibbs-Duhem relation we find

$$N_1 (\partial\mu_1/\partial N_1)_{V,\mu_s} = V (\partial P/\partial N_1)_{V,\mu_s}. \tag{A9}$$

Combining Eqs. [A6], [A7], [A8], and [A9] finally gives

$$\begin{aligned} \frac{V \overline{\Delta n^2}}{kT} = & (V^2 n_V^2 - \phi^2)\kappa + \frac{1}{V} \sum_{i,k=2}^m \gamma_i \gamma_k (\partial N_k/\partial\mu_i)_{V,\mu_s, N_1} \\ & + \frac{\sum_{i,k=1}^m \gamma_i \gamma_k \left(\frac{\partial N_k}{\partial N_1}\right)_{V,\mu_s} \left(\frac{\partial N_i}{\partial N_1}\right)_{V,\mu_s} N_1}{V^2 (\partial P/\partial N_1)_{V,\mu_s}}, \end{aligned} \tag{A10}$$

which gives Eq. [12] after conversion to concentrations $c_i = N_i/V$, making use of Eqs. [5] and [13], and writing Π for P . Indeed $V(\partial P/\partial N_1)_{V,\mu_s}$ or

$(\partial P/\partial c_1)_{\mu_s}$ represents the change in pressure of the colloidal solution, with the colloid concentration at constant chemical potentials of all other components, and this corresponds exactly with the change in the Donnan pressure of the colloidal solution.

APPENDIX II

ESTIMATION OF THE DIFFERENCE BETWEEN THE TURBIDITY CONTRIBUTED BY THE LOW MOLECULAR WEIGHT COMPOUNDS IN THE COLLOID-CONTAINING AND IN THE COLLOID-FREE SOLUTION

The difference between τ^*/A (see Eq. [19]) and the first and third term on the right-hand side of Eq. [12]

$$\frac{\tau^{0*}}{A} = [V^2 n_v^2 - \phi^2] \kappa + \sum_{i,k=2}^m \gamma_i \gamma_k (\partial c_i / \partial \mu_k)_{\mu_s, c_1} \quad [B1]$$

is caused by the presence of the colloid material with the concentration c_1 , and is in first approximation proportional to c_1 . The proportionality constant can be found by differentiating τ^{0*} with respect to c_1 at constant μ_s . It should then be compared to the proportionality constant of the main term

$$\left[\sum_{i=1}^m \gamma_i (\partial c_i / \partial c_1)_{\mu_s} \right]^2 / (\partial \Pi / \partial c_1)_{\mu_s}. \quad [B2]$$

Writing R for the ratio of $(\partial(\tau^{0*}/A)/\partial c_1)$ to [B2] and introducing concentrations by weight

$$g_i = c_i M_i / N_{Av}, \quad [B3]$$

where M_i is the molecular weight of component i , we find

$$R = \frac{\frac{N_{Av}}{M_1} \frac{\partial}{\partial g_1} \left\{ \left[V^2 \left(\frac{\partial n}{\partial V} \right)_N^2 - \left(\sum_{i=1}^m \left(\frac{\partial n}{\partial g_i} \right)_{P_0} g_i \right)^2 \right] \kappa + \sum_{i,k=2}^m \left(\frac{\partial n}{\partial g_i} \right)_{P_0} \left(\frac{\partial n}{\partial g_k} \right)_{P_0} \left(\frac{\partial g_i}{\partial \mu_k} \right)_{\mu_s, g_1} \frac{M_k}{N_{Av}} \right\}}{\left[\sum_{i=1}^m \left(\frac{\partial n}{\partial g_i} \right)_{P_0} \left(\frac{\partial g_i}{\partial g_1} \right)_{\mu_s} \right]^2 / \left(\frac{\partial \Pi}{\partial c_1} \right)_{\mu_s}}. \quad [B4]$$

A reasonable estimate of R can be obtained by the following simplifications and substitutions. All $(\partial n/\partial g_i)$ are taken as equal, independent of g_1 , and about equal to $+0.3$; $V(dn/dV)$ is of the same order, but negative: $\partial/\partial g_1[V(dn/dV)]$ can be estimated at about -0.1 ; $\sum_1^m (\partial g_i/\partial g_1)$, which includes the term $(\partial g_1/\partial g_1) = 1$ and the (negative) adsorptions $(\partial g_i/\partial g_1)_{i \neq 1}$, can be estimated at 0.5 or higher; $\partial \Pi/\partial c_1 = kT$; κ is equal to 5×10^{-11} ergs/cm.³ (for water) and $\frac{\partial \kappa}{\partial g_1}$ may vary between -5×10^{-11} and

$+5 \times 10^{-11}$. The term $\partial/\partial g_1 \sum_{i,k=2}^m (\partial g_i/\partial \mu_k)_{\mu_{i,g}}$ can be transformed as follows.

Neglecting activity corrections we put

$$\mu_k = \mu_k^0 + \nu_k kT \ln g_k^0,$$

where ν_k is a small integer and g_k^0 is the weight concentration in the equilibrium solution at $g_1 = 0$. Now

$$g_i = g_i^0 + \beta_i g_1,$$

where β_i depends on all g_i^0 's. In the more simple cases $\sum_i \beta_i$ will be a function of $\sum_2^m g_i^0$. At high electrolyte concentration it will reach a limit. At low electrolyte concentration it varies as (ionic strength)^{1/2} or as $(\sum_2^m g_i^0)^{1/2}$. With these assumptions the actual transformation is simple.

$$\begin{aligned} \frac{\partial}{\partial g_1} \sum_{i,k=2}^m (\partial g_i/\partial \mu_k)_{\mu_{i,g}} &= \sum \partial^2 (g_i^0 + \beta_i g_1) / \nu_k kT \partial g_1 \partial \ln g_k^0 \\ &= \frac{1}{\nu kT} \sum_k \frac{\sum \beta_i}{\partial \ln g_k^0} = \frac{1}{\nu kT} \frac{\partial \sum \beta_i}{\partial \ln \sum g_k^0} = \frac{1}{2} \frac{\sum \beta_i}{\nu kT}. \end{aligned} \quad [B5]$$

Here ν is a weighted average between the ν_k 's. Taking this as equal to 2 and taking -0.5 for $\sum \beta_i$ (cf. the value chosen for $\sum (\partial g_i/\partial g_1)$), R finally becomes

$$R = \frac{4RT}{M_1} \left(+3 \times 10^{-11} \pm 5 \times 10^{-11} - \frac{\overline{M}_k}{8RT} \right). \quad [B6]$$

With $RT = 2.5 \times 10^{10}$ this reduces to

$$R = +\frac{3}{M_1} \pm \frac{5}{M_1} - \frac{\overline{M}_k}{2M_1}. \quad [B7]$$

Therefore the absolute error introduced is at most of the order of the average molecular weight of the low molecular solutes and probably never less than 5 or 10 units in the molecular weight.

Finally, we remark that a very similar, if not identical value for R is found, if the differentiation of [B1] is not carried out at constant chemical potential, but at constant concentrations of the low molecular weight compounds.

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