mum suppressors are unnecessary for the elimination of anodic or cathodic maxima. The primary cathodic reaction in strong thiocyanate solution is the reversible reduction of gallium(III) to the metal, and the current is controlled by diffusion.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NORTH CAROLINA]

The Application of Light Scattering to the Study of the Hydrolytic Aggregation of Ions[1]

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The use of light scattering measurements on systems of polyelectrolytes in the presence of supporting electrolytes is discussed with particular emphasis on low molecular weight inorganic polymers of relatively high charge. Equations are developed for the determination of the degree of aggregation of charged species in the presence of supporting electrolyte. Estimates are made of the error caused by the assumption that the turbidities of the various components are additive under these conditions.

Although the theory of light scattering in multicomponent systems has been rather thoroughly discussed,[3-5] the application of light scattering measurements to the determination of molecular weights and degrees of aggregation of polymers with high charge to weight ratios has not been considered in detail.

Equations have been developed for the determination of molecular weights of charged protein molecules in the presence of supporting electrolyte[6]; however, the experimental conditions for the study of proteins are considerably different from those used in the study of ionic aggregation. The light scattering of these inorganic polyelectrolytes must be studied at relatively high concentrations to permit accurate turbidity measurements. This, in turn, necessitates the use of rather high concentrations of the supporting electrolyte. Since the differential refractive index of the supporting electrolyte is not negligible in comparison to that of the polymer, as is usually true with proteins, the contributions of all of the components in the system to the turbidity must be carefully considered. In many respects, this paper is a parallel of the discussion by Johnson, Kraus and Scatchard[7] of the application of sedimentation equilibrium in the ultracentrifuge to the study of similar systems.

Several workers have used light scattering measurements to determine approximate molecular weights of the isopoly and heteropoly acids and their salts[8-12] and aggregates formed by the hydrolysis of multivalent metal ions.[13]

It has been observed that the equation which describes the scattering in relatively dilute solutions of non-electrolytes

$$Hc/\tau = 1/M_w + 2Bc \qquad (1)$$

appeared to be obeyed when the measurements on the inorganic polyelectrolytes were made on solutions with a relatively large and constant concentration of supporting electrolyte.[11] Similar behavior also was observed with a large but variable concentration of supporting electrolyte.[12,13] In a study of the scattering by solutions of phosphotungstic acids,[10] it was observed that equation 1 failed, presumably because of charge effects. It was also observed that the scattering by these solutions followed equation 1 at very low values of the *p*H. This was probably a result of two factors, the reduction in charge of the species by protonation and also the presence of relatively high concentrations of the 1:1 supporting electrolyte $HClO_4$.

It has been suggested[10] that a separate determination of $(\partial \ln a_2/\partial c_2)$, where c_2 is the concentration in g./ml., by e.m.f. or isopiestic methods would allow the calculation of M_2 in a two component system when equation 1 is not obeyed, since the general relation describing the scattering in two component systems is given by the equation

$$\tau = \frac{HM_2}{(\partial \ln a_2/\partial c_2)} \qquad (2)$$

This method involves some difficulty in the separate determination of $(\partial \ln a_2/\partial c_2)$ which would limit it to very favorable systems.

In general light scattering measurements are most useful for studying systems at relatively high degrees of polymerization. The more usual methods of e.m.f. titrations, spectrophotometry, cryoscopy, etc., are particularly useful at the beginning of the aggregation where the degree of polymerization is low.

1. Turbidity of Multi-component Systems.—The equation for the turbidity τ in excess of that due to density changes, *i.e.*, in excess of that due to the scattering by the pure solvent, has been given by Stockmayer.[5]

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[11] U. P. Strauss, E. H. Smith and P. L. Wineman, *ibid.*, **75**, 3935 (1953).

[12] D. J. Bettinger and S. Y. Tyree, *ibid.*, **79**, 3355 (1957).

[13] (a) J. K. Ruff and S. Y. Tyree, *ibid.*, **80**, 1523 (1958); (b) **80**, 5654 (1958).

$$\tau = \frac{32\pi^3 n^2 kT}{3\lambda^4 N} V \sum_2^c{}_{\mathrm{i}} \sum_2^c{}_{\mathrm{j}} \frac{(\partial n/\partial m_{\mathrm{i}})(\partial n/\partial m_{\mathrm{j}})B_{\mathrm{ij}}}{|(\partial \mu_{\mathrm{i}}/\partial m_{\mathrm{j}})|} \tag{3}$$

n = refractive index of soln.
V = vol. of the solvent, component 1
B_{ij} = cofactor of the determinant $|(\partial\mu_{\mathrm{i}}/\partial m_{\mathrm{j}})|$
m = quantity of component i in the system. $|(\partial\mu_{\mathrm{i}}/\partial m_{\mathrm{j}})|$ represents the determinant of all $(\partial u_{\mathrm{i}}/\partial m_{\mathrm{j}})$, omitting the first component, the solvent

It is convenient to rewrite equation 3 in terms of the molarities of the components, assuming the volume fraction of component 1 to be unity. As suggested by Edsall, *et al.*,[6] the equation will be written in terms of the derivatives of the activities rather than the chemical potentials with respect to the molarities. This gives the equation for the turbidity

$$\tau = \frac{32000\pi^3 n^2}{3N\lambda^4} \sum_2^c{}_{\mathrm{i}} \sum_2^c{}_{\mathrm{j}} \frac{\psi_{\mathrm{i}}\psi_{\mathrm{j}}A_{\mathrm{ij}}}{|a_{\mathrm{ij}}|} \tag{4}$$

$$\psi_{\mathrm{i}} = (\partial n/\partial m_{\mathrm{i}}),\ A_{\mathrm{ij}} = \text{cofactor of } |a_{\mathrm{ij}}|$$

$$a_{\mathrm{ij}} = (\partial \ln a_{\mathrm{i}}/\partial m_{\mathrm{j}}) = a_{\mathrm{ji}}$$

a_{i} is the activity of the ith species. Grouping constant terms together, letting $H'' = 32000\pi^3 \cdot n^2/3N\lambda^4$

$$\tau = H'' \sum_2^c{}_{\mathrm{i}} \sum_2^c{}_{\mathrm{j}} \frac{\psi_{\mathrm{i}}\psi_{\mathrm{j}}A_{\mathrm{ij}}}{|a_{\mathrm{ij}}|} \tag{5}$$

2a. Equations for a Three Component System.—A three component system consisting of a solvent, a mono-disperse polymeric electrolyte and a supporting electrolyte will be considered. The general equation for scattering in a three component system has been given by Edsall, *et al.*[6]

$$\tau/H'' = \frac{\psi_2^2 a_{33} - 2\psi_2\psi_3 a_{23} + \psi_3^2 a_{22}}{a_{22}a_{33} - a_{23}^2} \tag{6}$$

If we designate the solvent, water, as component 1, the polymeric electrolyte PX_z as component 2, and the supporting 1:1 electrolyte BX as component 3, we may write down these expressions for the activities

$$\ln a_2 = \ln m_2 + \nu_{2\mathrm{a}} \ln m_{\mathrm{a}} + \beta_2$$
$$\ln a_3 = \nu_{3\mathrm{c}} \ln m_{\mathrm{c}} + \nu_{3\mathrm{a}} \ln m_{\mathrm{a}} + \beta_3$$

where

$\nu_{2\mathrm{a}}$ = no. of anions X^- in component 2
$\nu_{3\mathrm{c}}$ = no. of cations B^+ in component 3 = 1
$\nu_{3\mathrm{a}}$ = no. of anions X^- in component 3 = 1
m_{c} = total molarity of B^+
m_{a} = total molarity of X^-
β_{i} = ln γ_{i}, the logarithm of the activity coefficient of the ith species

It should be noted that although the following derivations are given in terms of a polymeric cation P^{z+} with univalent anions X^-, the treatment is symmetrical with respect to charge and applies equally well to the case of a polymeric anion P^{z-} with univalent cations B^+.

It has been found extremely advantageous to study these systems in a constant ionic medium, *i.e.*, with a high concentration of supporting electrolyte. This procedure has been used with e.m.f. and spectrophotometric measurements, sedimentation equilibrium in the ultracentrifuge, etc. This allows one to assume to a close approximation that activity coefficients remain constant during the measurements and reduces the number of variables by one-half.[14] Under these conditions, $(\partial\beta_{\mathrm{i}}/\partial m_{\mathrm{j}}) \simeq 0$. Taking derivatives of the activities, we obtain

$$a_{22} = 1/m_2 + \frac{\nu_{2\mathrm{a}}}{m_{\mathrm{a}}}\frac{\partial m_{\mathrm{a}}}{\partial m_2}$$

$$a_{33} = \frac{1}{m_{\mathrm{c}}}\frac{\partial m_{\mathrm{c}}}{\partial m_3} + \frac{1}{m_{\mathrm{a}}}\frac{\partial m_{\mathrm{a}}}{\partial m_3}$$

$$a_{23} = \frac{\nu_{2\mathrm{a}}}{m_{\mathrm{a}}}\frac{\partial m_{\mathrm{a}}}{\partial m_3}$$

$$m_{\mathrm{c}} = m_3,\ m_{\mathrm{a}} = m_3 + Z_2 m_2 \text{ since } \nu_{2\mathrm{a}} = Z_2$$

Since a_{23} is of the same order of magnitude as a_{22} and a_{33}, and ψ_3 is not negligible in comparison to ψ_2 as is the case with proteins in the presence of 1:1 electrolytes such as NaCl, the cross terms in equation 6 are not negligible. This makes it impossible to obtain a convenient expression for the turbidity in terms of the molecular weight of PX_z.

2b. Alternate Definition of Components.—In order to reduce the effect of variations in concentration of the supporting electrolyte on the activity of the polymeric component, a different set of components has been suggested by Scatchard[15] for use in the study of polyelectrolytes. These definitions also have been found useful in the study of sedimentation equilibrium in these systems[7] and in the study of light scattering by proteins.[6] Instead of defining the polymeric component as PX_z, one defines a new component 2, $PX_{z/2}B_{-z/2}$, *i.e.*, $PX_z - zBX/2$. The addition of one mole of component 2 to the solution gives one mole of particles, and the molecular weight of component 2 is $M_{PX_z} - (z/2)M_{BX_z}$. The molarity of component 2 is the same as with the previous definition; the activity is different. This also necessitates a redefinition of component 3 which now differs in molarity but not in activity from the previous definition. We may now write down the expressions for the activities

$$\ln a_2 = \ln m_2 + \nu_{2\mathrm{c}} \ln m_{\mathrm{c}} + \nu_{2\mathrm{a}} \ln m_{\mathrm{a}} + \beta_2$$
$$\ln a_3 = \nu_{3\mathrm{c}} \ln m_{\mathrm{c}} + \nu_{3\mathrm{a}} \ln m_{\mathrm{a}} + \beta_3$$

The constant ionic medium makes the assumption $(\partial\beta_{\mathrm{i}}/\partial m_{\mathrm{j}}) = 0$ valid to a close approximation, so these expressions are obtained

$$a_{22} = 1/m_2 + \frac{\nu_{2\mathrm{c}}}{m_{\mathrm{c}}}\frac{\partial m_{\mathrm{c}}}{\partial m_2} + \frac{\nu_{2\mathrm{a}}}{m_{\mathrm{a}}}\frac{\partial m_{\mathrm{a}}}{\partial m_2}$$

$$a_{23} = \frac{\nu_{2\mathrm{c}}}{m_{\mathrm{c}}}\frac{\partial m_{\mathrm{c}}}{\partial m_3} + \frac{\nu_{2\mathrm{a}}}{m_{\mathrm{a}}}\frac{\partial m_{\mathrm{a}}}{\partial m_3}$$

$$a_{33} = \frac{\nu_{3\mathrm{c}}}{m_{\mathrm{c}}}\frac{\partial m_{\mathrm{c}}}{\partial m_3} + \frac{\nu_{3\mathrm{a}}}{m_{\mathrm{a}}}\frac{\partial m_{\mathrm{a}}}{\partial m_3}$$

Also

$$m_{\mathrm{c}} = m_3 - Z_2 m_2/2,\ \nu_{2\mathrm{c}} = -Z_2/2,\ \nu_{3\mathrm{c}} = 1$$
$$m_{\mathrm{a}} = m_3 + Z_2 m_2/2,\ \nu_{2\mathrm{a}} = Z_2/2,\ \nu_{3\mathrm{a}} = 1$$

Setting $\eta = Z_2 m_2/2m_3$

$$a_{22} = 1/m_2 + Z_2^2/2m_3(1 - \eta^2) \tag{7}$$

$$a_{23} = \frac{-Z_2}{m_3}\left(\frac{\eta}{1 - \eta^2}\right) \tag{8}$$

$$a_{33} = 2/m_3(1 - \eta^2) \tag{9}$$

So long as Z_2 is relatively small and the measurements are made with dilute polymer solutions at

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(14) R. S. Tobias, *J. Chem. Educ.*, **35**, 592 (1958).

(15) G. Scatchard, THIS JOURNAL, **68**, 2315 (1946).

large values of m_3, $\eta \simeq 0$ and the cross term a_{23} in equation 6 vanishes. Then the turbidities become additive and

$$\tau/H'' = \frac{\psi_2{}^2}{1/m_2 + Z_2{}^2/2m_3(1 - \eta^2)} + \frac{\psi_3{}^2}{2/m_3(1 - \eta^2)} \quad (10)$$

Again so long as $(1 - \eta^2) \simeq 1$, the term $H'' \phi_3{}^2/2/m_3$ represents the turbidity of a solution of BX of concentration m_3. To a good approximation, a background experiment may be run on pure BX solutions to determine the contribution of the supporting electrolyte to the total turbidity of the solution containing the polymeric electrolyte. Subtraction of this background turbidity from the gross turbidity τ gives τ^*, a turbidity due to component 2. Converting from concentrations in moles/l. to g./cc. and assuming $(1 - \eta^2) = 1$, we obtain

$$\frac{\tau^*}{H'} = \frac{\varphi_2{}^2}{1/M_2c_2 + 1000Z_2{}^2/2m_3M_2{}^2}\,H' = 10^{-3}H''$$

φ_2 = wt. refractive index increment of component 2
c_2 = concn. of component 2 in g./cc.
M_2 = mol. weight of component 2

Letting $\varphi_2{}^2H' = H$, and rearranging

$$Hc_2/\tau^* = 1/M_2 + 1000Z_2{}^2c_2/2m_3M_2{}^2 \quad (11)$$

Thus so long as careful consideration is given to the turbidity of the constant ionic medium used as a solvent, *e.g.*, 1 *M* $NaClO_4$, a plot of Hc_2/τ^* *versus* c_2 should give a straight line when $(1 - \eta^2) \simeq 1$.

3. Scattering in Idealized Three Component Systems.—In order to determine the accuracy with which the molecular weights can be obtained using equation 11, turbidities were calculated for several idealized systems subject to the restrictions that the polymer is monodisperse, the volume fraction of the solvent is unity and the activity coefficients of all species are constant. The parameters were selected to simulate distribution of low molecular weight inorganic polymers, and systems were chosen which were similar to those used by Johnson, Kraus and Scatchard[7] to test the equations for distribution in a centrifugal field. For example, the value of $(\partial n/\partial m_3) = 0.01$ is similar to that for $NaClO_4$ which has been reported as 7.79×10^{-3} l./*M*.[16] The value of $(\partial n/\partial c)$ has been reported as 0.103 cc./g. for 12-phosphotungstic acid,[10] 0.174 cc./g. for the isopolymolybdates,[16] and 0.0957 cc./g. for the cationic aggregates formed by the hydrolysis of Al^{3+}.[13a]

The calculations were made by substituting the values of a_{22}, a_{33} and a_{23} calculated as a function of Z_2, m_2 and m_3, using equations 7, 8 and 9, into equation 6 and solving for τ. The constant value of the turbidity of the ionic medium τ_{BX} was obtained assuming it to be given by

$$\tau_{BX} = \frac{H''\psi_3{}^2}{2/m_3}$$

Calculations also were made assuming that the turbidity of the solutions in excess of that attributable to the supporting electrolyte of the ionic medium was given by the simple relation for a two component system, equation 2. This quantity is tabulated as τ_{PX_z}. The magnitude of the difference between $\tau_{PX_z} + \tau_{BX}$ and τ is a measure of the effect of the cross terms in equation 6 on the total turbidity. These data are presented in Table I.

TABLE I

SUMMARY OF THE RESULTS OF THE COMPUTATIONS OF THE TURBIDITY IN IDEALIZED 3-COMPONENT SYSTEMS

$(\partial n/\partial m_2) = 0.1$ $M_2 = 1000$ $n_{solv.} = 1.34$
$(\partial n/\partial m_3) = 0.01$ $M_3 = 100$ $\lambda = 4360$ Å.

mPX$_z$	η	$(1 - \eta^2)$	$\tau_{PX_z} \times 10^5$	$\tau \times 10^5$
$Z_2 = 4$, $m_3 = 3.00$, $\tau_{BX} = 4.28 \times 10^{-5}$				
0.300	0.200	0.960	46.6	55.3
.200	.133	.982	37.0	43.3
.100	.067	.996	22.5	27.4
.050	.033	.999	12.6	17.0
.025	.017	1.000	6.68	11.0
.0125	.0083	1.000	3.45	7.75
.0062	.0042	1.000	1.75	6.04
$Z_2 = 8$, $m_3 = 3.00$, $\tau_{BX} = 4.28 \times 10^{-5}$				
0.300	0.400	0.840	17.8	31.0
.200	.267	.929	17.3	26.2
.100	.133	.982	13.7	19.5
.050	.067	.996	9.28	14.1
.025	.033	.999	5.62	10.0
.0125	.0167	1.000	3.14	7.46
.0062	.0083	1.000	1.67	5.96
$Z_2 = 4$, $m_3 = 1.00$, $\tau_{BX} = 1.38 \times 10^{-5}$				
0.300	0.600	0.640	17.4	31.4
.200	.400	.840	19.0	25.9
.100	.200	.960	15.0	17.9
.050	.100	.990	9.83	11.6
.025	.050	.998	5.75	7.24
.0125	.025	.999	3.14	4.55
.0062	.012	1.000	1.64	3.03

The turbidity $\tau^* = \tau - \tau_{BX}$ is plotted *versus* c_2 in Fig. 1. It can be seen from Fig. 1 that the curvature of the Hc_2/τ^* *versus* c_2 plots caused by the non-additivity of the turbidities at the higher concentrations does not preclude a reasonably accurate extrapolation to infinitely dilute solutions. The molecular weight M_2 can be obtained with good accuracy. The curvature does render the measurement of the limiting slope less accurate and tends to lead to low values of Z_2.

4. Consideration of Complexes with Ions from the Constant Ionic Medium.—Some complexing of the polymeric electrolyte by ions of opposite charge from the constant ionic medium is to be expected, since these ions are present in a large excess. In general this effect is advantageous, since it reduces the charge on the polymeric species making the system more amenable to study. The light scattering measurements thus provide a means of measuring the interaction of the species with the constant ionic medium, data which cannot be obtained by equilibrium studies using e.m.f. measurements, etc.

When $\bar{\nu}$ ions of opposite charge to P^{z+} react to form a complex, the effective charge of the polymeric species is

$$Z_2{}^* = (Z_2 - \bar{\nu})$$

Component 2 is now redefined as $(PX_{\bar{\nu}})^{(Z-\bar{\nu})} + X_{(Z-\bar{\nu})} - (Z - \bar{\nu})BX/2$ or $PX_z - (Z - \bar{\nu})BX/2$. This necessitates a redefinition of component 3 as $m_3{}^* = m_3 - \bar{\nu}m_2/2$. The difference in $m_3{}^*$ and m_3

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[16] L. H. Jenkins, Ph.D. dissertation, Univ. of N. C., 1955.

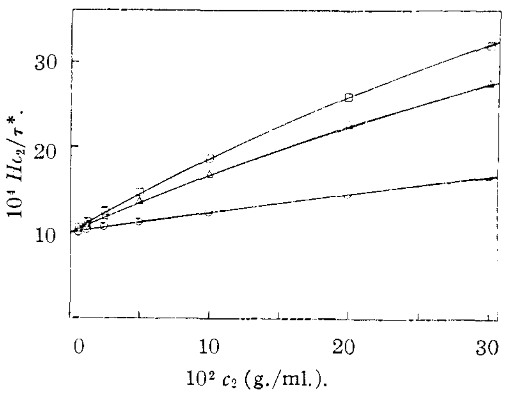

Fig. 1.—Test of the linearity of $(Hc_2/\tau^*(c_2))$: ○, $Z_2 = 4$, $m_3 = 3.00$; △, $Z_2 = 8$, $m_3 = 3.00$; □, $Z_2 = 4$, $m_3 = 1.00$.

is quite small, and both may be assumed equal to the concentration of the supporting electrolyte at low values of η. Substitution of the activities based on these definitions into the scattering equation gives a new set of equations differing only in the replacement of Z_2 by Z_2^* and m_3 by m_3^*. Thus

$$Hc/\tau^* = 1/M_2 + 1000Z_2^{*2}/2m_3^*M_2^2 \qquad (12)$$

In the study of ionic aggregation, it is convenient to define a monomeric unit as $[M(H)_{\bar{n}}X_{\nu}{}^{(Z+\bar{n}-\nu)+}$ $X_{(Z+\bar{n}-\bar{\nu})}$ where Z is the charge on the ion M and $\bar{n}$, the average number of hydrogen ions consumed per mole of M, may be obtained by electrometric titrations. The average number of X^- bound, $\bar{\nu}$, then may be calculated from the values of $Z_2^{*\prime}$, the average charge per monomer unit using the relation $Z_2^{*\prime} = Z_2^*/N$, where there are N monomer units in the polymer. Although it would appear that one could calculate values of M_2 from values of the slope of the Hc/τ^* *versus* c curve at different values of m_3^*, this is not generally possible since $\bar{\nu}$ is a function of m_3^*.

5. Equations for a Four Component System.—A four component system consisting of a solvent, a polymeric component and two supporting electrolytes HX and BX will be considered. In many systems, the ionic aggregation occurs at such low *p*H values that the free acid concentration cannot be neglected. The polymeric component 2 is assigned the formula

$$PX_{Z_2/2}H_{-Z_2m_3}/2(m_3 + m_5)B_{-Z_2m_5}/2(m_3 + m_5)$$

The supporting electrolytes HX and BX are components 3 and 5, respectively. The concentrations of the various ions are

$$m_P = m_2$$
$$m_H = m_3 - Z_2m_2m_3/2(m_3 + m_5) = m_3(1 - \eta^*)$$
$$m_B = m_5 - Z_2m_2m_5/2(m_3 + m_5) = m_5(1 - \eta^*)$$
$$m_X = m_3 + m_5 + Z_2m_2/2 = (m_3 + m_5)(1 + \eta^*)$$
$$\eta^* = Z_2m_2/2(m_3 + m_5)$$

With the same restrictions involving monodispersity, constancy of activity coefficients, as before, we obtain

$$a_{22} = 1/m_2 + Z_2^2/2(1 - \eta^{*2})(m_3 + m_5)$$
$$a_{33} = [2m_3 + m_5(1 - \eta^{*2})]/m_3(m_3 + m_5)(1 - \eta^{*2})$$
$$a_{55} = [2m_5 + m_3(1 - \eta^{*2})]/m_5(m_3 + m_5)(1 - \eta^{*2})$$
$$a_{35} = (1 + \eta^{*2})/(1 - \eta^{*2})(m_3 + m_5)$$

As was the case in the 3 component system, the terms involving the change in activity of component 2 with the concentration of component 3 or 5 are negligible with this definition of components if η^* is small. So long as these cross terms involving the polymer are negligible, the scattering equation for a 4 component system may be written as

$$\tau = \frac{H''\psi_2^2}{a_{22}} + \frac{H''(\psi_3^2a_{55} - 2\psi_3\psi_5a_{35} + \psi_5^2a_{33})}{(a_{33}a_{55} - a_{35}^2)} \qquad (13)$$

The second term in equation 13 is simply the turbidity of a mixture of m_3 moles/l. of HX and m_5 moles/l. of BX. This may be obtained by a background experiment and subtracted from the total turbidity of the solution to give the turbidity τ^* due to the polymeric component alone. Substituting the values of a_{22} into equation 13

$$Hc_2/\tau^* = 1/M_2 + 1000Z_2^2c_2/2M_2^2(m_3 + m_5)$$

This equation is the same as for the 3 component system, except for the replacement of m_3 by $(m_3 + m_5)$.

6. Equations for a System with Polydisperse Aggregates and One Supporting Electrolyte.—Applying the general equation for scattering in multi-component systems with the same restrictions of the constancy of activity coefficients, small values of $\Sigma_iZ_im_i/2m_3 = \eta'$, etc., we obtain

$$\tau^*/H'' = \Sigma_i\Sigma_j\psi_i\psi_jA_{ij}/|a_{ij}| \qquad (14)$$

τ^* is the turbidity corrected for that due to the supporting electrolyte, and the summation is extended over all even (polymeric) components. As before, we obtain

$$a_{ii} = 1/m_i + Z_i^2/2m_3(1 - \eta'^2)$$
$$a_{ij} = Z_iZ_j/2m_3(1 - \eta'^2)$$

where $i \neq j$. If the polymeric ions are of the type $M[M(H)_t]_n$ where t is a constant which may be + or − and n is variable, as has been observed by Sillén and co-workers[17] to be generally true in these systems, it seems likely that the weight refractive index increments φ_i will be approximately equal over a narrow range of n values. In this case converting to weight refractive index increments

$$10^3\tau^*/H'\varphi^2 = 10^3\tau^*/H = \Sigma_i\Sigma_jM_iM_jA_{ij}/|a_{ij}| \qquad (15)$$

Cross terms involving the polymeric components vanish only when the charge effects become negligibly small or in the limit as $c \rightarrow 0$. The weight average molecular weight of the polymeric components may be obtained by extrapolation to $c = 0$ in the usual manner, since

$$\lim_{c \to 0} Hc/\tau^* = \Sigma_ic_i/\Sigma_iM_ic_i = 1/M_w \qquad (16)$$

7. Computational Procedure.—In order to interpret the experimentally determined turbidity of solutions of cation or anion aggregates, the scattering is attributed to a polymeric species $([MH_{\bar{n}}\cdot X_{\bar{\nu}}]^{(z+\bar{n}-\bar{\nu})}X_{(z+\bar{n}-\bar{\nu})})_N$. N is defined as the weight average number of metal ions M in the polymeric species. The quantity $\bar{n}$ can be accurately determined by electrometric titrations. When the Sillén "core + links" mechanism is obeyed,[17] measurements at constant $\bar{n}$ correspond to measurements at constant composition of the system. Since z,

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(17) S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, **8**, 1607 (1954).

the charge on the cation or anion undergoing polymerization, and $\bar{n}$ are generally both known, the charge per monomer unit, $Z^{*\prime} = (z + \bar{n} - \bar{\nu})$, can only have values between $z + \bar{n}$ and 0. In order to obtain a system corresponding to the one treated in the hypothetical case, it is necessary to make the measurements at high values of $\bar{n}$. Under these conditions, ψ_2 is considerably greater than ψ_3, and since $\bar{n}$ will have a sign opposite to z the possible values of $Z^{*\prime}$ are limited to a narrow range. In addition, the use of a weakly complexing ionic medium like $NaClO_4$ makes it very unlikely that $\bar{\nu}$ will have values greater than about 0.5. In order to relate the properties of the monomeric component to those of the polymeric component, these quantities are defined

$$Z_2^*/N = Z^{*\prime}, \text{ charge per monomer unit} \quad (17)$$

$$M_2/N = M', \text{ formula wt. of the monomer component} \quad (18)$$

$$m_2 \cdot N = m', \text{ molarity of component 2 computed as monomer} \quad (19)$$

$$\psi' = (\mathrm{d}n/\mathrm{d}m') \quad (20)$$

Within the relatively narrow range of possible $Z^{*\prime}$ values, values of $Z^{*\prime}$ are assumed and used to calculate c_2, φ_2 and m_3^*. It is convenient to plot the deviation function obtained by substituting (17) and (18) in (12) and rearranging terms

$$\frac{Hc_2M'}{\tau^*} - \frac{10^3Z^{*\prime 2}c_2}{2m^*_3M'} = \frac{1}{N} = \frac{H''\psi'^2m'}{\tau^*} - \frac{Z'^2m'}{2m_3} \quad (21)$$

as a function of c_2 or m'. When the correct value of $Z^{*\prime}$ is chosen, the plot will have a limiting slope of 0 and an intercept $1/N$. This is shown in Fig. 2 in which the turbidity data for the first case in Table I which corresponds to the case with $N = 5$, $M' = 200$, and $Z^{*\prime} = 0.8$ are plotted as deviation functions. Values of M', c_2, m_3^* and φ_2 were computed for $Z^{*\prime} = 0.4$ and 1.2 in addition to the correct value 0.8. In this case, the value chosen for $Z^{*\prime}$ has a significant effect on the value of N; however, the large deviations from 0 slope obtained with incorrect $Z^{*\prime}$ values make a fairly accurate estimate of the charge possible. It should be noted that while deviations from equation 12 limit the accuracy of the determination of $Z^{*\prime}$, the effect of $Z^{*\prime}$ on the intercept decreases rapidly and eventually becomes negligible as the ratio ψ_2/ψ_3 increases. The analysis of highly polydisperse systems is restricted to those where $\psi_2 >> \psi_3$ and $Z^{*\prime}$ is best set equal to 0 in the calculation of N_w.

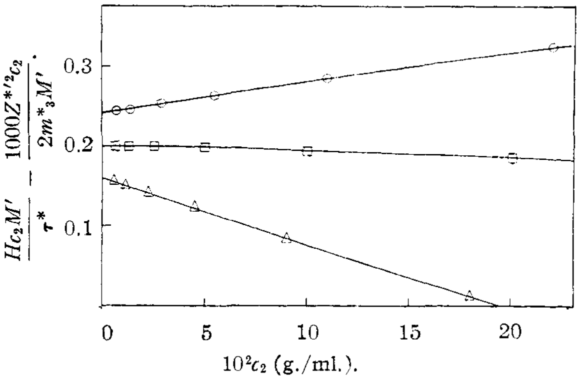

Fig. 2.—Effect of $Z^{*\prime}$ on the determination of N: ○, $Z^{*\prime} = 0.4$; □, $Z^{*\prime} = 0.8$; △, $Z^{*\prime} = 1.2$.

In summary it has been shown that the average degree of polymerization N may be calculated from light scattering measurements on systems at high values of $\bar{n}$. Since N and $Z^{*\prime}$ may also be obtained from sedimentation equilibrium measurements, a system may be studied by two independent experimental methods. Light scattering measurements provide a means of obtaining information about systems at high values of N where data from the more usual e.m.f. and cryoscopic measurements tend to be inconclusive and also provide a convenient method for measuring the aggregation as a function of time in systems where the equilibria are not attained rapidly.

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Kinetics of the Formation of the Ferric Chloride Complex

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A previously described apparatus for rapidly mixing two solutions has been used to study the kinetics of the reaction: $Fe^{+++} + Cl^- = FeCl^{++}$ in aqueous solution. The forward rate law has been determined to be $\mathrm{d}(FeCl^{++})/\mathrm{d}t = k_1(Fe^{+++})(Cl^-) + k_2[(Fe^{+++})(Cl^-)/(H^+)]$. At 25° and an ionic strength of 1.0 M the values of k_1 and k_2 are 9.4 ± 1.0 M^{-1} sec.$^{-1}$ and 18.0 ± 2.0 sec.$^{-1}$, respectively. The heats and entropies of activation were calculated from the variation of the rate with temperature. Mechanisms for the observed rate law are discussed and the rate constants and entropies of activation are compared with those for the analogous thiocyanate reaction. A lower limit for the rate of chloride complexing of iron(III) in 3 M sodium chloride has been obtained from nuclear magnetic resonance studies and compared with the results of the spectrophotometric kinetics studies.

The reaction in aqueous solution of ferric ion with chloride ion to form the monochloride complex $FeCl^{+2}$ is known to be rapid, but apparently no quantitative study of the rate had been made previously. The present work constitutes a determination of the rate law using the fast mixing apparatus which had been applied earlier to the study of the kinetics of the analogous complexing reaction of thiocyanate ion with ferric ion.[1]

Chloride Complexing Constants.—In the interpretation of the data it is necessary to know the equilibrium quotients relating the various species

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[1] J. F. Below, R. E. Connick and C. P. Coppel, THIS JOURNAL **80**, 2961 (1958).