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Effect of the Third Virial Coefficient on the Intensity of Light Scattered by Mixed Aqueous Solution of Poly(vinylpyrrolidone) and Sodium Dodecyl Sulfate

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It was found that the reduced intensity of scattered light, R_θ, increases and then decreases with polymer concentration, becoming maximum for a certain concentration of the polymer, when the third virial coefficient, A_3, is positive. The theoretical concentration of polymer for the maximum R_θ is $(3A_3M_2)^{-1/2}$, where M_2 is the molecular weight of the polymer. This was observed in the case of the aqueous solution of poly(vinylpyrrolidone) (PVP) mixed with sodium dodecyl sulfate (SDS). In the mixed solution, PVP and SDS form a complex which behaves like a polyelectrolyte with or without a simple salt of low concentration. Such a solution often has higher-order virials. The value of the polymer concentration for the maximum scattered light intensity agreed with the theoretical value.

Turbidity or intensity of scattered light increases, for the first approximation, in proportion to the concentration of colloidal or macromolecular solutes. This is utilized as a method of chemical analysis such as nephelometry of turbidimetry. According to the fluctuation theory, however, the intensity of scattered light does not necessarily increase but sometimes decreases with the solute concentration under certain conditions. The possibility of decrease of turbidity with increase of polymer concentration is of particular interest in relation to physiological problems such as the transparency of eye lenses. The lens of a human eye is transparent in the normal condition of water content (62%), but the lens becomes turbid when the content of water increases to 80—90%. Thus the lens of high content of macromolecules (protein) is less turbid than that of low content of the protein.

In this paper, the effect of solute concentration on the reduced intensity of the scattered light is discussed theoretically and the results are compared with those obtained by using the mixed system of poly (vinylpyrrolidone) (PVP) and sodium dodecyl sulfate (SDS) in aqueous solution.

Theoretical

The reduced scattering intensity, R_θ, for unpolarized incident beam is defined as follows:

$$R_\theta = \left(\frac{r^2 I_\theta}{I_0}\right) \Big/ (1+\cos^2\theta), \tag{1}$$

where r is the photometric distance, and I_0 and I_θ are the intensity of the incident light and scattered light, respectively, per unit volume at the scattering angle of θ. The term $(r^2 I_\theta/I_0)$ is the Rayleigh ratio.

According to fluctuation theory, the intensity of the scattered light depends on the fluctuation both of the density of solvent and of the concentration of solute. The former component is assumed to be constant regardless of solute concentration when solute concentration is sufficiently low. The latter component of the reduced intensity of the scattered light, R_θ, is proportional both to $(\partial\pi/\partial c_2)^{-1}$ and to $(\partial n_{12}/\partial c_2)^2$, where π is the osmotic pressure, n_{12} the refractive index of the solution, and c_2 the concentration of the solute. Thus,

$$\frac{Kc_2}{R_\theta} = \frac{1}{RT}\cdot\frac{\partial\pi}{\partial c_2}, \tag{2}$$

where R and T are the gas constant and the absolute temperature, respectively, of the solution. K is a constant defined as follows:

$$K = 2\pi^2 n_1^2 \left(\frac{\partial \bar{n}_{12}}{\partial c_2}\right)^2 \Big/ N_\mathrm{A}\cdot\lambda_0^4, \tag{2-a}$$

where N_A is the Avogadro number, n_1 the refractive index of the solvent, and λ_0 the wavelength of the incident beam *in vacuo*. The left-hand side of Eq. 2 is, therefore, a quantity which can be determined as a function of θ and c_2.

The interference factor, $P(\theta)$, should be introduced into the equation of R_θ when the light scattering by large particle is considered. By expanding both terms $(\partial\pi/\partial c_2)$ and $P(\theta)$ in power series, we obtain the following equation which is used to analyse the data of the light scattering in a polymer solution:[1]

$$\frac{Kc_2}{R_\theta} = \frac{1}{M_2}\left(1+\frac{16\pi^2 n_1^2}{3\lambda_0^2}\langle R_\mathrm{G}^2\rangle \sin^2(\theta/2)\right) + 2A_2c_2, \tag{3}$$

where M_2 is the molecular weight of the solute (polymer), $\langle R_\mathrm{G}^2\rangle$ the mean-square value of the radius of gyration of polymer coil in the solution, and A_2 the second virial coefficient.

When the scattering angle, θ, is zero, the interference factor is equal to unity. In order to consider the effect of polymer concentration, the term $(\partial\pi/\partial c_2)$ in Eq. 2 is expanded to the third virial, and we obtain[2,3]

$$Kc_2/R_0 = \frac{1}{M_2} + 2A_2c_2 + 3A_3c_2^2, \tag{3-a}$$

where A_3 is the third virial coefficient. From this, the reduced intensity, R_0, of the scattered light at $\theta=0°$ is given by

$$R_0 = Kc_2 \Big/ \left(\frac{1}{M_2}+2A_2c_2+3A_3c_2^2\right), \tag{4}$$

and the differential of R_0 by c_2 by

$$\frac{\partial R_0}{\partial c_2} = \frac{K\left(\frac{1}{M_2}-3A_3c_2^2\right)}{\left(\frac{1}{M_2}+2A_2c_2+3A_3c_2^2\right)^2}. \tag{5}$$

Case 1: When $A_2=0$ and $A_3=0$, Eqs. 4 and 5

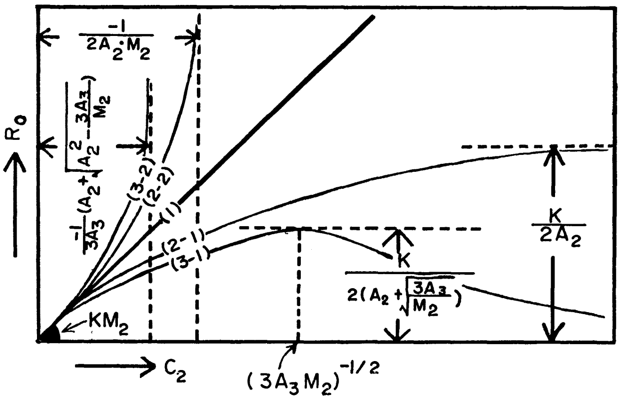


Fig. 1. Schematic diagram for the relationship between the reduced intensity of the scattered light, R_0, and solute concentration, c_2.
curve(1): $A_2=0$ and $A_3=0$, (2-1): $A_2>0$ and $A_3=0$,
(2-2): $A_2<0$ and $A_3=0$, (3-1): $A_2 \geqq 0$ and $A_3>0$
(3-2): $A_2 \leqq 0$ and $A_3<0$:

become as follows:

$$R_0 = KM_2c_2, \tag{6}$$

$$\frac{\partial R_0}{\partial c_2} = KM_2. \tag{7}$$

The relationship between R_0 and c_2 is shown in Fig. 1 as straight line (1), the slope of which is KM_2 as shown by Eq. 7.

Case 2: When $A_2 \neq 0$ and $A_3=0$, Eqs. 4 and 5 become as follows:

$$R_0 = Kc_2 \Big/ \left(\frac{1}{M_2}+2A_2c_2\right), \tag{8}$$

$$\frac{\partial R_0}{\partial c_2} = \left(\frac{K}{M_2}\right) \Big/ \left(\frac{1}{M_2}+2A_2c_2\right)^2. \tag{9}$$

In this case, R_0 increases monotonically with c_2. The initial slope (slope at $c_2 \to 0$) is KM_2 as in case 1. If A_2 is positive, R_0 and $\partial R_0/\partial c_2$ approach $K/(2A_2)$ and zero, respectively, with increasing c_2. On the other hand, if A_2 is negative, both R_0 and $\partial R_0/\partial c_2$ diverge to infinity when c_2 approaches $-1/(2A_2M_2)$. These relationships are shown in Fig. 1 by curves (2-1) and (2-2) for $A_2>0$ and <0, respectively.

Case 3: When $A_3 \neq 0$, the initial slope for the relationship between R_0 and c_2 is KM_2 as in cases 1 and 2. If $A_3>0$ and $A_2 \geqq 0$, R_0 has a maximum value, according to Eq. 5, where

$$c_{2,\max} = (3A_3M_2)^{-1/2}, \tag{10}$$

and

$$R_{0,\max} = \frac{K}{2\left(A_2+\sqrt{\frac{3A_3}{M_2}}\right)}. \tag{11}$$

This relation is shown by curve (3-1) in Fig. 1. Thus, the reduced intensity of the scattered light, R_0, decreases in spite of the increase in the concentration of polymer, c_2, when c_2 is larger than $c_{2,\max}$. This is in contrast to the case $A_3=0$ in cases 1 and 2. If $A_3<0$ and $A_2 \leqq 0$, both R_0 and $\partial R_0/\partial c_2$ tend to infinity at

$$c_2 = -\frac{1}{3A_3}\left(A_2+\sqrt{A_2^2-\frac{3A_3}{M_2}}\right). \tag{12}$$

This relation is also shown by curve (3-2) in Fig. 1.

From Eq. 4, the specific reduced intensity of the scattered light R_0/c_2 is given by

$$\frac{R_0}{c_2} = K \Big/ \left(\frac{1}{M_2}+2A_2c_2+3A_3c_2^2\right), \tag{13}$$

and its differential by the solute concentration $\partial(R_0/c_2)/\partial c_2$ by

$$\frac{\partial}{\partial c_2}\left(\frac{R_0}{c_2}\right) = \frac{-2K(A_2+3A_3c_2)}{\left(\frac{1}{M_2}+2A_2c_2+3A_3c_2^2\right)^2}. \tag{14}$$

According to Eq. 13, R_0/c_2 becomes KM_2 irrespective of the values of A_2 and A_3 when c_2 approaches zero. As for the inclination of the (R_0/c_2) *vs.* c_2 curves given by Eq. 14,

$$\frac{\partial}{\partial c_2}(R_0/c_2) = 0, \tag{15}$$

for $A_2=0$ and $A_3=0$, and R_0/c_2 is constant regardless of the value of c_2. When $A_2>0$ and $A_3 \geqq 0$, we have

$$\frac{\partial}{\partial c_2}(R_0/c_2) < 0, \tag{16}$$

and R_0/c_2 decreases monotonically with c_2, while for $A_2<0$ and $A_3 \leqq 0$,

$$\frac{\partial}{\partial c_2}(R_0/c_2) > 0, \tag{17}$$

and R_0/c_2 increases monotonically with c_2.

Straight line (1) shows the proportionality of the scattering intensity R_0 to the polymer concentration c_2. Thus, R_0/c_2 becomes constant. This is in the case of a solution with θ-solvent.

Curves (2-1) and (3-1) show the dependence of the scattering intensity, R_0, on the polymer concentration, c_2, in a good solvent. In these cases, the polymer coil expands enough and the degree of fluctuation of concentration is relatively small, because of positive A_2 and A_3 in a good solvent. R_0, shown by curve (2-1) or (3-1), therefore, deviates negatively from the straight line (1) in Fig. 1, R_0/c_2 decreasing with c_2. Particularly in the case of curve (3-1) where A_3 is not equal to zero but positive, the repulsion between expanded polymer coils suppresses the concentration fluctuation so that the scattering intensity decreases with the increase of the polymer concentration at high concentration region.

Curves (2-2) and (3-2), on the other hand, show the dependency of R_0 on c_2 in a poor solvent. R_0 deviates positively from the straight line (1) and R_0/c_2 increases with c_2 because of the negative values of A_2 and A_3 and the large fluctuation in a poor solvent. Both the reduced intensity and the specific reduced intensity of the scattered light tend to infinity at a critical polymer concentration. This is the critical opalescence due to the two-phase separation of the polymer solution at the polymer concentration higher than the critical value.

So far, only typical conditions for the real solution have been considered. From a mathematical viewpoint, other conditions such as $A_2>0$ and $A_3<0$, or $A_2<0$ and $A_3>0$, should be considered, but discussion was not made.

Experimental

Material and Solution. Poly(vinylpyrrolidone) (hereafter called PVP) and sodium dodecyl sulfate(SDS) are the same as those reported.[4] The materials were dissolved in twice distilled water. The molecular weight of PVP, M_P, was kept constant throughout the experiment, but that of complex, M_{complex}, changed with the concentration of SDS; the relation is given by Eq.19-a.

The membrane equilibrium should be attained before the measurement since PVP and SDS form a complex in aqueous solution, the complex behaving like a polyelectrolyte.[5] Visking Cellulose Tubing was used with an initial inner solution of PVP mixed with SDS, and initial outer solution of SDS. The method of the membrane equilibrium is the same as that reported.[4]

After the membrane equilibrium has been attained, a solution of concentration of PVP–SDS complex, c_{complex}, at a given concentration of free SDS, c_s^f, can be prepared, if the outer solution is used as a solvent or as a diluting agent for the inner solution of PVP–SDS complex, since chemical potential of SDS in the inner solution is equal to that in the outer solution at the membrane equilibrium. The amount of SDS bound to PVP of unit weight can also be kept constant when c_s^f is kept constant through the dilution process. A solution, in which the amount of SDS is bound to PVP at the membrane equilibrium, can be prepared by adjusting the concentration of SDS of both sides of the membrane before the membrane equilibrium is attained. The dependence of the scattering intensity, R_θ, both on the scattering angle, θ, and on the concentration of complex, c_{complex}, was measured under the conditions of a constant concentration of free SDS, c_s^f. This system will be called the dialysed system.

The same measurement was carried out under the conditions of a constant concentrations of total SDS, c_s^t, in order to compare the results with those of the dialysed system. Concentration c_s^t indicates the sum of concentrations of free SDS and of bound SDS in a solution of PVP mixed with SDS. This system will be called the undialysed system.

Measurements of the Reduced Intensity of Scattered Light and the Increment of Refractive Index. Methods of measurement of refractive index increment are the same as those reported.[4] In order to measure the scattering intensity, a Shimadzu Electrophotometric Light Scattering Photometer PG-21 was used at 436 nm and at 25 °C. The reduced intensity of the scattered light, R_θ, is experimentally given as follows.

$$R_\theta = \phi_\theta \frac{G_\theta}{G_0} \tag{18}$$

where G_θ and G_0 are intensity of electric current in a phototube at scattering angle of θ and of zero degree, respectively. ϕ_θ is an empirical coefficient depending both on a scattering angle, θ, and the refractive index of the solvent, n_1.[6]

Results

Dependence of the Reduced Intensity of Scattered Light on Polymer Concentration. The concentrations of PVP and the PVP–SDS complex are denoted by c_P and c_{complex}, respectively, in order to distinguish them from the concentration of "polymer," c_2. The relationship between c_P and c_{complex} is given by

$$c_{\text{complex}} = (1+y)c_p, \tag{19}$$

where y is the weight of SDS bound per unit weight of PVP. The relationship between the molecular weight of PVP, M_P, and that of the complex, M_{complex}, is given by

$$M_{\text{complex}} = (1+y)M_p \tag{19-a}$$

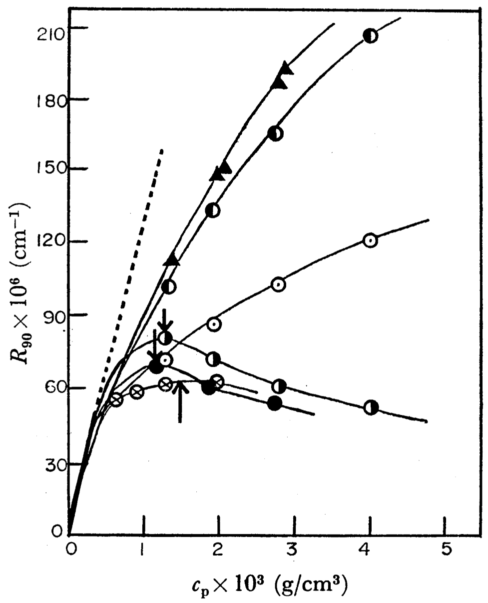
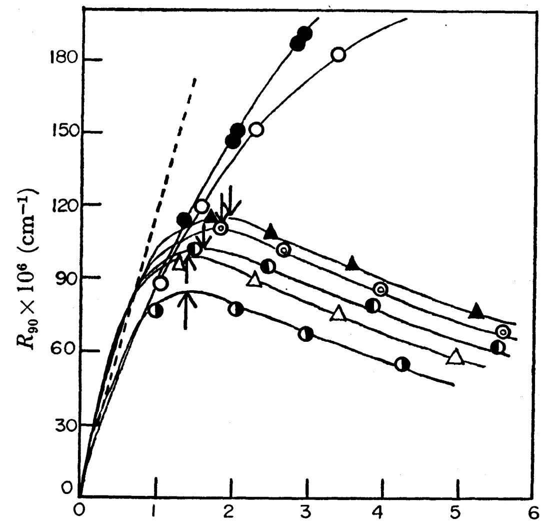


Fig. 2. Relationship between concentration of PVP, c_p and reduced intensity of scattered light at 90°, R_{90}. These are undialysed systems, and each concentration of total SDS, c_s^t, is kept constant through the measurement. Concentration of total SDS, c_s^t(mM): ▲ 0.0, ◐ 2.0, ⊙ 4.0, ⊗ 6.0, ● 8.0, ◑ 10.0.

Empirical relationship between PVP concentration, c_P, and the reduced intensity of the scattered light measured at 90°, R_{90}, are given in Fig. 2, where total concentration of SDS, c_s^t, is kept constant. This is the result obtained by the undialysed system. When c_s^t is small, *viz.*, in the case of 0 mM(▲), 2 mM(◐), and 4 mM(⊙), R_{90} increases with c_P, but when c_s^t is large, *viz.*, in the case of 6 mM(⊗), 8 mM(●) and 10 mM(◑), R_{90} decreases in spite of the increase in c_P. In the case of the undialysed system in which c_s^t is kept constant throughout the measurement (Fig. 2), it should be noted that PVP and SDS form a complex with each other, so that M_{complex} as well as the amount of SDS bound per unit weight of PVP, y, decrease with c_p. It is thus difficult to analyse the effect of c_s^t, c_{complex}, and M_{complex} on the reduced scattering intensity, R_{90}, and to explain the results. However it may be emphasized that the anomalous decrease of the scattered light intensity with the increase in the polymer concentration is observed even under simple experimental conditions.

On the other hand, it is easy in the case of the dialysed system to analyse the change of R_{90} with the concentration of PVP, c_P, since the free concentration of SDS, c_s^f, the amount of bound SDS, y, and the molecular weight of the complex, M_{complex}, can be kept constant throughout the measurement of R_{90}.

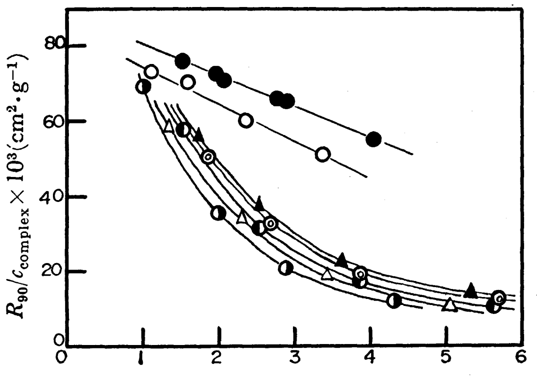
Since the value of y as a function of c_s^f is known,[4,5] the relationship between R_{90} and c_{complex} can be obtained (Fig. 3). Each symbol indicates the experimental value. When c_s^f is large, R_{90} decreases in spite



$c_{\text{comlex}}\times 10^3$ (g/cm^3)

Fig. 3. Relationship between complex concentration, c_{comlex}, and reduced intensity of scattered light at 90°, R_{90}. These results are of the dialysed system, and concentration of free SDS, $c_s{}^f$, is kept constant through the measurement. Each arrow mark shows the maximum point of each curve, which is calculated by Eq. 10 as same as in the case of Fig. 2. The dotted line shows the initial slope for the aqueous solution of PVP without SDS.

Concentration of free SDS, $c_s{}^f$(mM): ● 0.00, ○ 2.00, ◑ 5.37, △ 6.82, ◐ 8.68, ◎ 15.58, ▲ 19.16.



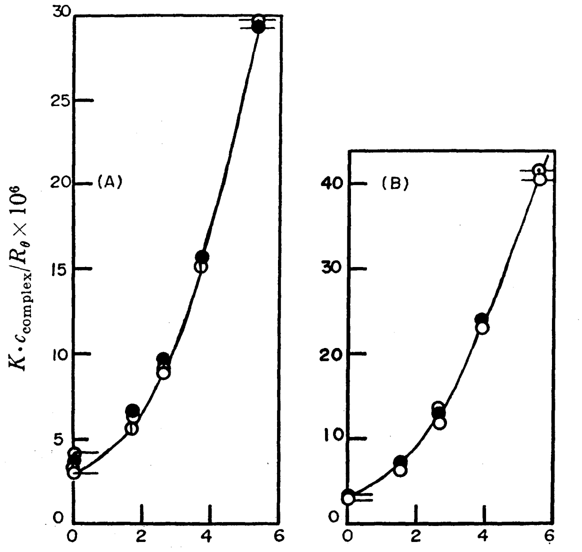
$c_{\text{complex}}\times 10^3$ (g/cm^3)

Fig. 4. Relationship between concentration of complex, c_{complex}, and specific reduced intensity of scattered light, $R_{90}/c_{\text{complex}}$. These results are of the dialysed system.

Concentration of free SDS, $c_s{}^f$(mM): ● 0.00, ○ 2.00, ◑ 5.37, △ 6.82, ◐ 8.68, ◎ 15.58, ▲ 19.16.

of the increase in the concentration of the complex, c_{complex}, in the region of high concentration of c_{complex} as in the case of the undialysed system (Fig. 2). The anomalous behavior can thus be observed in both the dialysed and undialysed systems.

The relationship between the specific reduced intensity of the scattered light, $R_{90}/c_{\text{complex}}$, and c_{complex} is shown in Fig. 4 on the basis of the data of Fig. 3 for the dialysed system. In the case of low concentration of free SDS, $c_s{}^f$, such as 0 mM(●) and 2 mM(○), $R_{90}/c_{\text{complex}}$ decreases linearly with c_{complex}, but in the case of high concentration of free SDS, such as 5.37 mM(◑) and higher, $R_{90}/c_{\text{complex}}$ decreases rapidly even in the region of low concentration of the complex, c_{complex}. Neither a maximum nor a minimum like that shown in Fig. 3 can be observed. The theoretical deduction has been verified experimentally.



$c_{\text{complex}}\times 10^3$ (g/cm^3) $c_{\text{complex}}\times 10^3$ (g/cm^3)

Fig. 5. Relationship between concentration of complex, c_{complex}, and $Kc_{\text{complex}}/R_\theta$. Different angles of the scattering, θ, are shown by different symbols. The solid line is the theretical curves calculated by Eq. 3-a.

Curve: (A)$c_s{}^f=19.16$mM, (B)$c_s{}^f=8.68$mM. Scattering angle: ○ 0°, ⦶ 45°, ● 90°, ⊙ 135°.

Dependence of Kc_2/R_θ on c_2 at Various θ. Dependence of Kc_2/R_θ on c_2 is shown in Fig. 5 for the dialysed system, for given θ-values as $\theta=0°$(○), 45°(⦶), 90°(●) and 135°(⊙), where the data at $\theta=0°$ is quoted from the Zimm Plot for the solution of PVP-SDS complex.[7] The pairs of short bars in Fig. 5, drawn at both the lowest and highest concentration of the complex, show the range of $Kc_{\text{complex}}/R_\theta$ from $\theta=0°$ through $\theta=135°$ at the respective complex concentrations. We see that the effect of θ is relatively small, the dependence of $Kc_{\text{complex}}/R_\theta$ on c_{complex} being approximately independent of θ. The conclusion is also applicable to the other data of both the dialysed and undialysed systems not shown in Fig. 5. The shapes of the curves show that the virial coefficients A_2 and A_3 of Eq. 3-a are both positive.

Discussion

Determination of Virial Coefficients, A_2 and A_3. Eq. 3-a can be rewritten as follows for the experimental determination of A_2 and A_3:

$$\frac{1}{c_2}\left(\frac{Kc_2}{R_0}-\frac{1}{M_2}\right)=2A_2+3A_3c_2. \tag{20}$$

Virial coefficients, A_2 and A_3, can thus be determined from a linear relationship between $(Kc_2/R_0-1/M_2)/c_2$ and c_2.

In the case of the dialysed system such as shown in Fig. 6, the subscript "2" in Eq. 20 should be read as

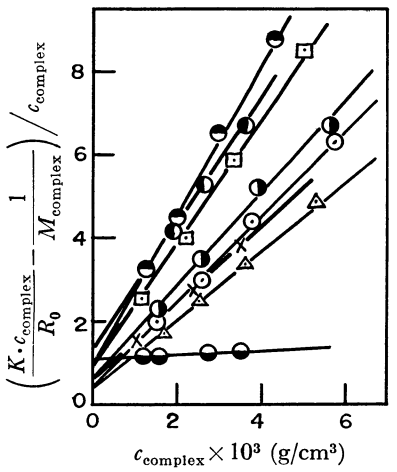


Fig. 6. The relationship between $c_{complex}$ and $(Kc_{complex}/R_0 - 1/M_{complex})/c_{complex}$. Both A_2 and A_3 can be estimated from the intercept and the slope of each straight line, as shown in Eq. 20. These results are for the dialysed system.
Concentration of free SDS(mM): ⊖ 2.00, ◐ 3.73, ◓ 5.37, ⊡ 6.82, ◑ 8.68, ⊙ 10.64, × 13.40, △ 19.16.

the subscript "complex." The free concentration of SDS, c_s^f, is kept constant for each line, all lines in Fig. 6 being straight. The virial coefficients, A_2 and A_3, are thus obtained for each concentration of free SDS, c_s^f, for each molecular weight of the complex. A_2 and A_3 are of the PVP–SDS complex in aqueous solution of free SDS.

On the other hand, in the case of the undialysed system, subscript "2" in Eq. 20 should be assumed to be "p". The relationship between $(Kc_P/R_0 - 1/M_P)/c_P$ *vs.* c_P at constant c_s^t becomes a straight line as in the case of the dialysed system (Fig. 6), in spite of the variation in the molecular weight of the complex when c_P changes at constant c_s^t. Apparent values of A_2 and A_3 are determined from these straight lines.

The dependence of A_2 and A_3 on c_s^f for the dialysed system(●) and that of the apparent A_2 and A_3 on c_s^t for the undialysed system(⊙) are shown in Fig. 7. In the region of low concentration of SDS, c_s^f or c_s^t, the third virial coefficient, A_3, is negligible, increasing with SDS concentration (Fig. 7). This is of particular interest, since the positive third virial coefficient is responsible for the anomalous decrease in R_0 or R_θ with the increase in c_2.

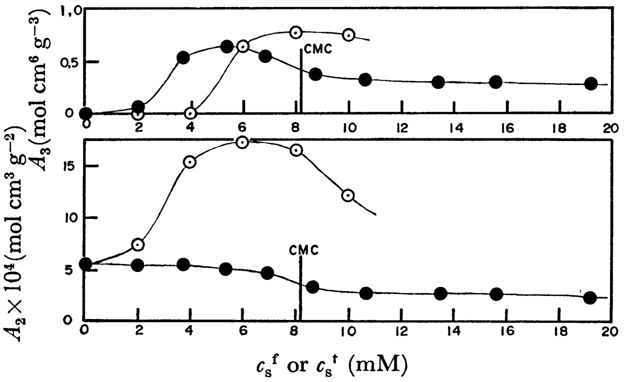


Fig. 7. The relationship between virial coefficients, A_2 or A_3, and concentration of SDS, c_s^f or c_s^t, for dialysed and undialysed system, respectively.
⊙ Undialysed system *versus* c_s^t, ● dialysed system *versus* c_s^f.

Comparison of Observed R_{90} with Calculated R_0. A comparison between experimental R_{90}-values and theoretical R_0-values is made herewith on the basis of the results where the effect of θ on R_θ is small (Fig. 5).

Solid curves in Figs. 2, 3, and 5 indicate the theoretical value of R_0 calculated by means of Eq. 4 using the values of A_2 and A_3 given in Fig. 7. Arrows (↑) in Figs. 2 and 3 show the maximum value of the reduced scattering intensity calculated by Eqs. 10 and 11. Agreement of the experimental R_{90}-values with the theoretical R_0-curves, and of the experimental maximum values with the theoretical ones (arrows) is good. It can therefore be concluded that the anomalous behaviour in Figs. 2 and 3 can be explained as the contribution of the third virial coefficient to the reduced scattering intensity.

The maximum point of the curve for $c_s^f = 2$ mM of the dialysed system is not shown in Fig. 3, since the concentration of the complex at the maximum point is higher because of the smallness of A_3. In the case of 0 mM of c_s^f, that is an aqueous solution of PVP without SDS, R_{90} or R_0 increases with the polymer concentration ($c_{complex}$ on the abscissa should read c_P in this case) and does not have a maximum point since A_3 is zero and the curve corresponds to curve (2-1) in Fig. 1. Broken lines in Figs. 2 and 3 indicate initial slopes for the curve of 0 mM of SDS (*i.e.* aqueous solution of PVP without SDS). Even when A_3 is zero, deviation from the broken line increases with the polymer concentration because of the contribution of the effect of the second virial coefficient, A_2. The initial slope, KM_2, is constant for all the curves in Figs. 1 and 2, since the molecular weight is assumed to be constant (M_2 or M_P). However, the initial slopes for the curves in Fig. 3, $KM_{complex}$, are variable and not constant since the molecular weight of the complex, $M_{complex}$, depends on the amount of SDS bound to PVP, y, which also depends on the concentration of free SDS, c_s^f, as shown by Eqs. 19 and 19-a. Thus, the initial slope, $KM_{complex}$, depends on y or c_s^f. The initial slope for the respective curves are not shown in Fig. 3 in order to avoid confusion.

Estimation of the Effect of the Interference Factor. In a rigorous sence it is wrong to compare R_{90} with R_0, since R_{90} is not equal to R_0 due to the interference factor, $P(\theta)^{-1}$. The effect of $P(\theta)^{-1}$, given by the following equation or the term in parenthesis on the right-hand

$$P(\theta)^{-1} = 1 + \frac{16\pi^2 n_1^2}{3\lambda_0^2}\langle R_G^2\rangle \sin^2(\theta/2), \qquad (21)$$

side of Eq. 3, should be evaluated at $\theta = 90°$ of the present experimental conditions in order to check the difference between R_{90} and R_0.

Assuming that θ is equal to 90° and a radius of gyration of PVP, $\langle R_G^2\rangle^{1/2}$, in water is 210 Å,[6,7] Eq. 21 is evaluated to be 1.12. The maximum value of $\langle R_G^2\rangle^{1/2}$ of the complex of PVP–SDS is *ca.* 1.5 times that of PVP in water, since the intrinsic viscosity of the complex at the highest amount of SDS bound to PVP is 3.5 times that of PVP in water.[5] Assuming that $\theta=90°$ and $<R_G^2>^{1/2}=315$ Å, the value of Eq. 21 is found to be 1.27. Thus, $1.12 \leqq P(90°)^{-1} \leqq 1.27$.

The relative difference of $Kc_{\text{complex}}/R_{90}$ against Kc_{complex}/R_0 is, therefore, assumed to be greater than 12% and less than 27% in the region of very low concentration of the polymer. However, in the region of high concentration of the polymer, the relative difference decreases with polymer concentration, because of the contribution of higher order virials such as $2A_2c_{\text{complex}}$ and $3A_3c_{\text{complex}}^2$ as shown by Eqs. 3 and 3-a. All the data of θ (Fig. 5) lie nearly on the theoretical curve for $\theta=0°$ calculated by means of A_2 and A_3 and Eq. 3-a. We might compare the experimental results obtained for $\theta=90°$ with the theoretical ones deduced for $\theta=0°$.

Comparison of the Theory of Debye and Bueche with Ours. Debye and Bueche[8] showed that R_θ increases and then decreases with c_2, and the concentration of polymer at the maximum value of R_θ is proportional to $M_2^{-1/2}$, not depending on the virial coefficients. However, the second and third virial coefficients are important for expressing the concentration, $c_{2,\text{max}}$, of the maximum value, $R_{0,\text{max}}$, of the reduced scattering intensity, as shown by means of Eqs. 10 and 11.

References

1) M. Nakagaki and H. Inagaki, "Experiments in Light Scattering (Kosanran Zikkenho)," Chaps. 1 and 2, Nankodo, Tokyo (1965).

2) C. Tanford, "Physical Chemistry of Macromolecules," John-Wiley, New York (1967), p. 287, 307.

3) Japan Chemical Society, "Shin Zikken Kagaku Koza, Light, part II," Maruzen, Vol. 4, Tokyo (1976), p. 737.

4) M. Nakagaki and S. Shimabayashi, *Nippon Kagaku Kaishi*, **1976**, 757.

5) M. Nakagaki and S. Shimabayashi, *Nippon Kagaku Kaishi*, **1972**, 1496.

6) M. Nakagaki, S. Shimabayashi, S. Yoshida, and M. Saito, *Yakugaku Zasshi*, **96**, 757 (1976).

7) M. Nakagaki and S. Shimabayashi, *Nippon Kagaku Kaishi*, to be published.

8) P. Debye and A. M. Bueche, *J. Chem. Phys.*, **18**, 1423 (1950).