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Isotropic Rayleigh Light Scattering in Two-component Systems. The Interdependence of the Concentration and the Density Scattering

Yoshinobu SHIOKAWA and Shin SUZUKI

The Research Institute for Iron, Steel and Other Metals, Tohoku University, Katahira 2-chome, Sendai 980

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The isotropic Rayleigh ratios in two-component systems are discussed in terms of the fluctuation of the thermodynamic quantities. It is found that the isotropic Rayleigh ratio, R_{is}, is the sum of the concentration scattering, R_c, due to fluctuation of the concentration and the so-called density scattering, R_d:

$$R_{is} = R_c + R_d$$

Thus, the cross-term of the concentration scattering and the density scattering, suggested by Bullough, is not included in the above expression. Our conclusion is confirmed by the determination of the molecular weight of sucrose.

The light-scattering measurements have been mainly applied to macromolecules. In the last decade, however, several papers have appeared with relation to small molecules, *e.g.*, the determination of the activity coefficient in a binary solution[1,2] and of the degree of polymerization for the hydrolysis product of metal ions.[3,4]

According to Einstein,[5] the isotropic Rayleigh ratio of liquid in the direction perpendicular to the incident light beam is given by:

$$R_{is} = \left(\frac{\pi^2}{2\lambda^4}\right)V\overline{(\Delta\varepsilon)^2} \tag{1}$$

where λ is the incident wavelength and $\overline{(\Delta\varepsilon)^2}$ is the mean square fluctuation in the dielectric constant in the region of a certain volume, V.

In a pure liquid the scattering of light is called the density scattering because the density fluctuation makes predominant contributions to the dielectric-constant fluctuation.[6]

The scattering of light in a solution is attributed not only to the density scattering, R_d, but also to the concentration scattering, R_c, arising from the concentration fluctuation:[7]

$$R_{is} = R_d + R_c \tag{2}$$

Thus, the isotropic Rayleigh ratio in a solution has been considered as the sum of these two contributions.

On the other hand, Bullough,[7–9] and Sicotte and Rinfret[10] have suggested such an expression for the isotropic Rayleigh ratio in two-component systems; their expression contains a cross-term, R'', besides those two contributions:

$$R_{is} = R_d + R'' + R_c \tag{3}$$

The cross-term makes a significant contribution to the isotropic Rayleigh ratio when both components of a solution have a low molecular weight.

Most of the published papers on the determination of the activity coefficient have taken the cross-term, R'', into account. Later, Sicotte,[11] and Segudovic and Deželič[12] have made theoretical considerations of this cross-term.

The purpose of the present work is to reexamine Bullough's theory. Therefore, we will discuss the isotropic Rayleigh ratio in two-component systems in terms of the statistical fluctuation concept and will determine the molecular weight of sucrose on the basis of our consideration.

The scattering of light in an aqueous sucrose solution has been studied by Debye,[13] by Halwer,[14] and by Maron and Lou.[15] Debye and Halwer made an inadequate calibration of the instrument, however, nor did they make any correction for the depolarization. Moreover, Maron and Lou made mistakes in their correction for the depolarization.

Theoretical

It is necessary to estimate the fluctuations of the thermodynamic quantities so as to ascertain the fluctuation of the dielectric constant in a solution.

Consider a small part of a two-component system containing a given number, N_0, of moles of a solvent. The probability function for the thermodynamic quantities is given by:[16]

$$\omega = C\exp\left[-\frac{1}{2kT}(\Delta S\Delta T - \Delta V\Delta P + \Delta N\Delta\mu)\right] \tag{4}$$

where ΔS, ΔT, ΔV, ΔP, ΔN, and $\Delta\mu$ are the fluctuations of the entropy, the temperature, the volume, the pressure, the number of moles of the solute, and the chemical potential of the solute respectively, and where C is a normalization constant.

Now, choose P, T, and N as independent variables. By expanding ΔS, ΔV, and $\Delta\mu$ near the equilibrium state as a series, we obtain:

$$\omega = C\exp\left[-\frac{1}{2kT}\left\{-\left(\frac{\partial^2 G}{\partial P^2}\right)(\Delta P)^2 - 2\left(\frac{\partial^2 G}{\partial P\partial T}\right)(\Delta P\Delta T) - \left(\frac{\partial^2 G}{\partial T^2}\right)(\Delta T)^2 + \left(\frac{\partial^2 G}{\partial N^2}\right)(\Delta N)^2\right\}\right] \tag{5}$$

where G is Gibbs' free energy. This relation means that the fluctuation of number of moles of the solute and the pressure or the temperature are statistically independent:

$$\overline{(\Delta N\Delta P)} = \overline{(\Delta N\Delta T)} = 0 \tag{6}$$

We thus have:

$$\overline{(\Delta P)^2} = -kT(\partial^2 G/\partial T^2)/D$$

$$\overline{(\Delta P\Delta T)} = kT(\partial^2 G/\partial T\partial P)/D$$

$$\overline{(\Delta T)^2} = -kT(\partial^2 G/\partial P^2)/D$$

$$\overline{(\Delta N)^2} = kT/(\partial^2 G/\partial N^2)$$

where:

$$D = (\partial^2 G/\partial T^2)(\partial^2 G/\partial P^2) - (\partial^2 G/\partial P \partial T)^2$$

Using the well-known thermodynamic transformations, we obtain:

$$\overline{(\Delta P)^2} = -kT(\partial P/\partial V)_{S,N} \tag{7}$$

$$\overline{(\Delta P \Delta T)} = kT^2(\partial P/\partial T)_{V,N}/C_V \tag{8}$$

$$\overline{(\Delta T)^2} = kT^2/C_V \tag{9}$$

$$\overline{(\Delta N)^2} = kT/(\partial \mu/\partial N)_{T,P} \tag{10}$$

where C_V is the specific heat at a constant volume. Equations (7), (8), and (9) are quite similar to those for one-component systems.16)

By expanding the dielectric constant as a series, we obtain:

$$\Delta\varepsilon = (\partial\varepsilon/\partial P)_{T,N}\Delta P + (\partial\varepsilon/\partial T)_{P,N}\Delta T + (\partial\varepsilon/\partial N)_{T,P}\Delta N$$

Considering Eq. (6), we find the mean squares of the fluctuation of the dielectric constant:

$$\overline{(\Delta\varepsilon)^2} = \left[\left(\frac{\partial\varepsilon}{\partial P}\right)^2_{T,N}\overline{(\Delta P)^2} + 2\left(\frac{\partial\varepsilon}{\partial P}\right)_{T,N}\left(\frac{\partial\varepsilon}{\partial T}\right)_{P,N}\overline{(\Delta T \Delta P)} + \left(\frac{\partial\varepsilon}{\partial T}\right)^2_{P,N}\overline{(\Delta T)^2}\right] + \left(\frac{\partial\varepsilon}{\partial N}\right)^2_{T,N}\overline{(\Delta N)^2} \tag{11}$$

By substituting $\overline{(\Delta P)^2}$, $\overline{(\Delta P \Delta T)}$, $\overline{(\Delta T)^2}$, and $\overline{(\Delta N)^2}$ into the above equation, we obtain:

$$\overline{(\Delta\varepsilon)^2} = \frac{kT}{V\beta_T}\left(\frac{\partial\varepsilon}{\partial P}\right)^2_{T,N}\left[1+\left(\frac{\beta_T}{\beta_S}-1\right)\chi^2\right] + \frac{kT}{(\partial\mu/\partial N)_{T,P}}\left(\frac{\partial\varepsilon}{\partial N}\right)^2_{T,P} \tag{12}$$

$$\chi = 1 + \frac{\beta_T(\partial\varepsilon/\partial T)_{P,N}}{\alpha_P(\partial\varepsilon/\partial P)_{T,N}}$$

where β_T is the isothermal compressibility, β_S is the adiabatic compressibility, and α_P is the isobaric expansivity.

Since we consider only a small part of the solution containing a given number, N_0, of moles of the solvent, we can regard the fluctuation of the number of moles of the solute as that of the concentration. From Eqs. (1) and (11), the expression for the isotropic Rayleigh ratio of the solution is the sum of the concentration scattering, R_c, due to the fluctuation of the concentration and the so-called density scattering, R_d, which is independent of the fluctuation of the concentration:

$$R_{is} = R_c + R_d \tag{13}$$

By using the $\varepsilon = n^2$ relationship, where n is the refractive index, we obtain:

$$R_c = \left(\frac{2\pi^2 kT}{\lambda^4}\right)Vn^2\left(\frac{\partial n}{\partial N}\right)^2_{P,T}\Bigg/\left(\frac{\partial\mu}{\partial N}\right)_{P,T} \tag{14}$$

$$R_d = \left(\frac{2\pi^2 kT}{\lambda^4\beta_T}\right)n^2\left(\frac{\partial n}{\partial P}\right)^2_{T,N}\left[1+\left(\frac{\beta_T}{\beta_S}-1\right)\chi^2\right] \tag{15}$$

Equation (15) is the same one as that shown by Coumou *et al.* for a pure liquid.6) Consequently, we can regard the isotropic Rayleigh ratio in a solution as being additively composed of concentration scattering and the so-called density scattering.

Experimental and Results

Experimental. The light-scattering measurements were made with light with a wavelength of 436 nm using a Shimadzu electrophotometric light-scattering photometer, PG-21. The photometer was calibrated using benzene, so as to obtain 47.5×10^{-6} cm^{-1} for the total Rayleigh ratio.17) This benzene was washed with concentrated sulfuric acid, passed through an activated aluminum oxide column, and carefully distilled prior to use. Measurements of the redistilled water used gave values for the Rayleigh ratio of 2.70×10^{-6} cm^{-1} and for the depolarization of 0.10. The aqueous sucrose solutions were purified by passing them through an activated carbon column15) and were then tested for dissymmetry. The total Rayleigh ratio, R_t, and the depolarization, ρ, were determined for the sucrose solution thus obtained. Each sample was filtered directly into the cell through a Millipore filter 220 or 100 nm in pore diameter under the pressure of nitrogen.

The refractive index increments were determined at 25 °C using a Shimadzu photoelectric differential refractometer, DR-3, calibrated with aqueous solution of sodium chloride.18)

The sucrose concentration was determined with both the density and the refractive index.18)

Results. The isotropic Rayleigh ratio was found by19)

$$R_{is} = \frac{6-7\rho}{6+6\rho}R_t \tag{16}$$

The so-called density scattering, R_d, of the sucrose solution was assumed to be equal to the isotropic Rayleigh ratio of water. The concentration scattering, R_c, was obtained by subtracting the isotropic Rayleigh ratio of water from the isotropic Rayleigh ratio, R_{is}, obtained by Eq. (16). The Rayleigh ratios, R_t, R_{is}, and R_c, for sucrose solutions which were obtained in this way are shown in Fig. 1. The variation in Δn for sucrose solutions is shown in Fig. 2, where Δn is the difference between the refractive index of a sucrose solution and that of water.

We can obtain the molecular weight of a solute by means of the following equations:

$$Hc/R_c = 1/M + 2Bc$$

$$H = (2\pi^2 n^2/\lambda^4 N_A)(\partial n/\partial c)^2_{P,T}$$

where c is the weight of a solute per ml of solution and B is the virial coefficient.

Figure 3 shows the plot of Hc/R_c for the sucrose concen-

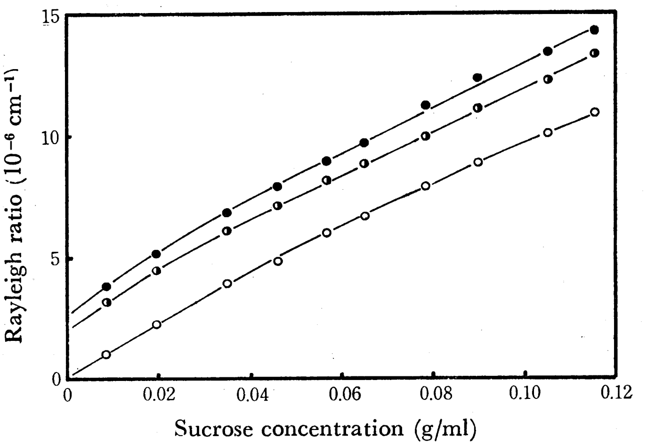

Fig. 1. Rayleigh ratio for aqueous sucrose solutions. ●: R_t, ◑: R_{is}, ○: R_c.

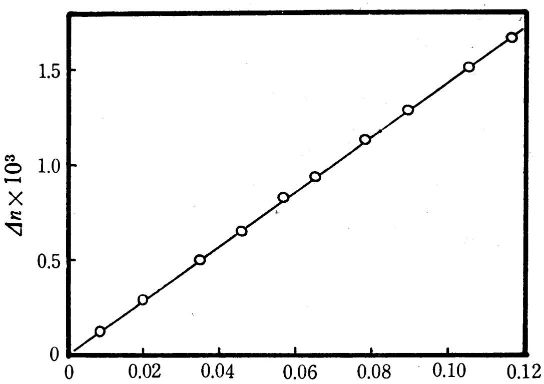

Fig. 2. Refractive index increment of aqueous sucrose solution.

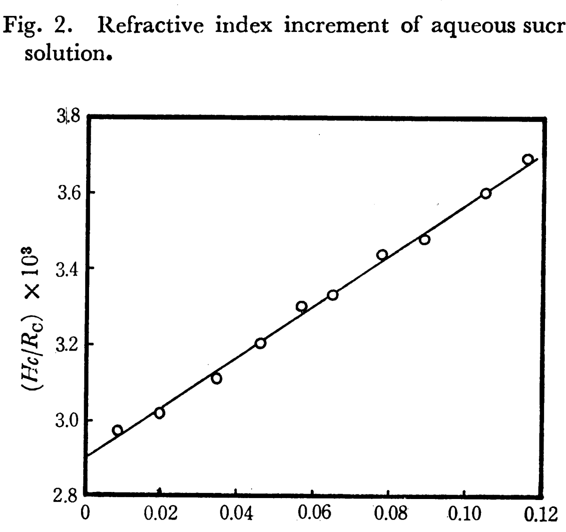

Fig. 3. Molecular weight determination of sucrose.

tration. This curve yields 344±6 as the molecular weight for sucrose, against a calculated value of 342.3.

Discussion

The good agreement of our experimental result with the calculated value confirms that the isotropic scattering is additively composed of the concentration scattering, R_c, and the so-called density scattering, R_d. This confirmation is also supported by the experimental results of Coumou and Mackor[1] and of Pethica and Smart.[20]

To elucidate the relationship between Eq. (3), which has been suggested by Bullough *et al.*, and our Eq. (13), we will express the fluctuation of the dielectric constant in terms of the density, the temperature, and the concentration thus:

$$\Delta\varepsilon = (\partial\varepsilon/\partial d)_{T,N}\Delta d + (\partial\varepsilon/\partial T)_{d,N}\Delta T + (\partial\varepsilon/\partial N)_{d,T}\Delta N \tag{17}$$

The density is given by $d=(N+N_0)/V$. We thus obtain:

$$\Delta d = -\frac{d}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}\Delta P - \frac{d}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N}\Delta T + \left(\frac{\partial d}{\partial N}\right)_{P,T}\Delta N \tag{18}$$

Using Eqs. (6), (7), (8), (9), and (10), we obtain:

$$\overline{(\Delta d)^2} = -kT\left(\frac{d}{V}\right)^2\left(\frac{\partial V}{\partial P}\right)_{T,N} + kT\left(\frac{\partial d}{\partial N}\right)^2_{P,T}\Big/\left(\frac{\partial \mu}{\partial N}\right)_{P,T} \tag{19}$$

$$\overline{(\Delta d\Delta T)} = 0 \tag{20}$$

$$\overline{(\Delta N\Delta d)} = kT\left(\frac{\partial d}{\partial N}\right)_{P,T}\Big/\left(\frac{\partial \mu}{\partial N}\right)_{P,T} \tag{21}$$

Equations (10), (19), and (21) are equivalent to Eqs. (2.10), (2.12), and (2.9) in Ref. 21 respectively. Relation (20) shows that the fluctuations in the temperature and the density are statistically independent. However the fluctuations in the concentration and the density are not independent.

From Eq. (17), we obtain:

$$\overline{(\Delta\varepsilon)^2} = \left(\frac{\partial\varepsilon}{\partial T}\right)^2_{d,N}\overline{(\Delta T)^2} + \left(\frac{\partial\varepsilon}{\partial d}\right)^2_{T,N}\overline{(\Delta d)^2} + 2\left(\frac{\partial\varepsilon}{\partial d}\right)_{T,N}\left(\frac{\partial\varepsilon}{\partial N}\right)_{T,d}\overline{(\Delta d\Delta N)} + \left(\frac{\partial\varepsilon}{\partial N}\right)^2_{d,T}\overline{(\Delta N)^2} \tag{22}$$

It is easily shown that this relation is equivalent to Eq. (11). This relation means that the isotropic Rayleigh ratio is represented by Eq. (3) under the assumption that $(\partial\varepsilon/\partial T)_{d,N}=0$, an assumption which Bullough *et al.*[7–9,11,12] implicitly made use of. In this case, the concentration scattering is given by:

$$R_c = \left(\frac{2\pi^2 kT}{\lambda^4}\right)Vn^2\left(\frac{\partial n}{\partial N}\right)^2_{d,T}\Big/\left(\frac{\partial \mu}{\partial N}\right)_{P,T} \tag{23}$$

However, the refractive index increment, $(\partial n/\partial N)$, is measured the pressure and the temperature being kept constant, while the density and the temperature are not. Unfortunately, attention has not been paid to this in several published papers.

It is clear from the above discussion that the isotropic Rayleigh ratio must be expressed by Eq. (13).

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