Supporting Information

Multiple Association–Dissociation Equilibria in Solutions of Amphiphilic Molecules

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SCATTERING METHOD FOR ANALYZING THE MULTIPLE EQUILIBRIA

Weight Average Aggregation Number. The (time-averaged) excess Rayleigh ratios $R_{\theta}$ for static light scattering (SLS) are measured experimentally as functions of the solute mass concentration $c$ and the scattering angle $\theta$. The angular dependence of $R_{\theta}$ is usually expressed in terms of the magnitude of the scattering vector defined by

$$k = \frac{4\pi n_{\text{solv}}}{\lambda_0} \sin \left( \frac{\theta}{2} \right)$$  \hspace{1cm} (S1)

Here, $\lambda_0$ is the wavelength of the incident light in vacuo, and $n_{\text{solv}}$ is the refractive index of the
solvent. The scattering power of the scattering component is determined by the refractive index increment $\frac{\partial n}{\partial c}$, and $R_\theta$ is analyzed using the optical constant $K$ defined by

$$K \equiv \frac{4\pi^2 n_{\text{solv}}^2}{N_A \lambda_0^4} \left( \frac{\partial n}{\partial c} \right)^2$$

where $N_A$ is the Avogadro constant. When the solution contains multiple scattering components with different scattering powers, $\frac{\partial n}{\partial c}$ is replaced by the weight averaged one $(\frac{\partial n}{\partial c})_{av} = \sum_i w_i (\frac{\partial n}{\partial c})_i$, where $w_i$ and $(\frac{\partial n}{\partial c})_i$ are the weight fraction and $\frac{\partial n}{\partial c}$ of the component $i$, respectively. Here, we consider only solutions containing scattering components with the same $\frac{\partial n}{\partial c}$, for simplicity.

According to the fluctuation theory of light scattering, the excess zero-scattering-angle Rayleigh ratio $R_0$ ($R_\theta$ at $\theta = 0$) of multicomponent solutions is formally written as

$$R_0 = R \frac{RT}{Kc} \sum_{m,n} \Delta_{mn}$$

where $\Delta_{mn}$ and $|\mu|$ are the cofactor and determinant, respectively, of the matrix whose $mn$ element is given by

$$\mu_{mn} \equiv \frac{1}{M_m} \left( \frac{\partial \mu_m}{\partial c_n} \right)$$

with the molar mass $M_m$ and chemical potential $\mu_m$ of the scattering component $m$, and the mass concentration $c_n (= M_n[U_n])$ of the scattering component $n$. The double summation in eq S3 are taken over all the scattering components.
For the ideal solution, $\mu_m$ is given by eq 4, where $[U_m] = c_m/M_m$, and $\mu_{mn}$ is calculated as

$$
\mu_{mn} = \frac{RT}{M_m c_m} \delta_{mn}
$$

(S5)

Using this equation, eq S3 gives us the result

$$
\frac{R_0}{Kc} = \sum_m w_m M_m = M_w
$$

(S6)

with the weight fraction $w_m (= c_m/c)$ of the component $m$. Thus, we can determine the weight average molar mass $M_w$ (or the weight average aggregation number $m_w$) of the solute (micelle) by SLS.

However, if the solution is not ideal, we must consider the inter-particle interference effect on the scattering intensity. Using the third virial approximation, $\mu_m$ is given by eq 19, and eq S3 provides the result

$$
\frac{Kc}{R_0} = \frac{1}{M_w} + 2A_{2,z} c + \left[ 2A_{3,z} + A_{3,w} - \left( \overline{A_{2,z}^2} - A_{2,z}^2 \right) M_w \right] c^2
$$

(S7)

with

$$
\left\{
A_{2,z} = M_w^{-1} \sum_m w_m M_m A_{2,mm}, \quad A_{2,z}^2 = M_w^{-1} \sum_m w_m M_m A_{2,mm}^2
\right. \\
A_{3,z} = M_w^{-1} \sum_m w_m M_m A_{3,mmm}, \quad A_{3,w} = \sum_m w_m A_{3,mmm}
$$

(S8)

At the infinite dilution, eq S7 tends to eq S6.

For cylindrical micellar solutions with finite concentrations, $\mu_m$ is given by eq 33, and eq S3 provides the result

S3 provides the result
\[
\frac{Kc}{R_0} = \frac{1}{M_w} + 2A_{2,\text{app}}(\phi)c
\] (S9)

where \(A_{2,\text{app}}(\phi)\) is the concentration dependent apparent second virial coefficient, of which explicit form is given by ref. 5. To obtain eq S9, we neglected terms on the order of \(m_0/m\) and higher in \(\mu_{mn}\), assuming cylindrical micelles in the solution are long enough. Equation S9 tends to eq S6 with decreasing \(c\) or \(\phi\), but \(M_w\) depends on the surfactant concentration for the cylindrical micellar solution, so that \(M_w\) at infinite dilution is not equal to that at finite concentrations. One must analyze SLS data at finite concentrations using eq S9 to obtain \(M_w\) or \(m_w\) at the corresponding concentrations.

**Radius of Gyration.** At finite scattering angles and when the scattering component size is comparable to the wavelength of light, the intra-particle interference effect becomes important. The excess Rayleigh ratio \(R_\theta\) at a finite \(\theta\) or \(k\) and concentration \(c\) can be formulated based on the Ornstein-Zernike integral equation theory (using the single-contact approximation). Neglecting the scattering component dependence of the virial coefficients, the theory gives us the equation\(^1\text{,6}\)

\[
\frac{Kc}{R_0} = \frac{1}{M_w^2 P_z(k)} + 2A_{2,\text{app}}(\phi)c
\] (S10)

where \(P_z(k)\) is the z-average particle scattering factor defined by

\[
P_z(k) = M_w^{-1} \sum_m w_m M_m P_m(k) = 1 - \frac{1}{3} \langle S^2 \rangle_z k^2 + O(k^4)
\] (S11)
with the particle scattering function $P_m(k)$ of the component $m$, and $\langle S^2 \rangle_z$ is the $z$-average mean-square radius of gyration given by

$$\langle S^2 \rangle_z = M_w^{-1} \sum_m w_m M_m \langle S^2 \rangle_m$$

(S12)

with the mean-square radius of gyration $\langle S^2 \rangle_m$ of the component $m$. To obtain $\langle S^2 \rangle_z$ at finite concentrations, we have to know $A_{2,\text{app}}(\phi)$.

**Dynamic Light Scattering (DLS).** The dynamic light scattering (DLS) experiment provides us the autocorrelation function $g^{(2)}(t)$ of the scattering intensity, which is in general written as

$$\left[ \frac{g^{(2)}(t) - 1}{g^{(2)}(0) - 1} \right]^{1/2} = \sum_i A(\tau_i, k) \exp \left( -\frac{t}{\tau_i} \right)$$

(S13)

where $t$ is the delay time of the correlation function, $\tau_i$ and $A(\tau_i, k)$ are the $i$-th relaxation time and its relaxation strength at $k$, respectively, and $A(\tau, k)$ is normalized as

$$\sum_i A(\tau_i, k) = 1$$

(S14)

The spectrum of $A(\tau, k)$ is obtained by the CONTIN analysis with choosing a suitable number of the relaxation times.

DLS measurements for micellar solutions often provide binodal spectrum of $A(\tau, k)$ (e.g., Figure 13b in the text), and we can divide the excess Rayleigh ratio $R\theta$ obtained by SLS into the fast and slow relation components by
Furthermore, using \( A(\tau, k) \), we can calculate the first cumulants of the fast and slow relaxation components by

\[
\Gamma_\alpha = -\lim_{t \to 0} \frac{d}{dt} \ln \left( \sum_{i \in \alpha} A(\tau_i, k) \exp \left( -\frac{t}{\tau_i} \right) \right) = \frac{\sum \tau_i^{-1} A(\tau_i, k)}{\sum A(\tau_i, k)} \quad (\alpha = \text{fast, slow})
\]  

(S16)

If the slow relaxation component is much bigger and has much higher molar mass than the fast relaxation component, the former scattering power is much stronger than the latter. Thus, when \( A(\tau, k) \) is bimodal, the contribution of the slow relaxation component to the scattering intensity is comparable (often even predominant) to that of the fast relaxation component, but the weight fraction of the slow relaxation component is much smaller (often negligible) than the fast relaxation component.

In such a case, we can obtain the following approximate equations\(^7,8\)

\[
\frac{R_{\theta, \text{fast}}}{Kc} \approx \frac{M_{w, \text{fast}} P_{z, \text{fast}}(k)}{1 + 2 A_{2, \text{fast}} M_{w, \text{fast}} P_{z, \text{fast}}(k)c}, \quad \frac{R_{\theta, \text{slow}}}{Kc} \approx \frac{R_{0, \text{slow}}}{Kc} P_{z, \text{slow}}(k)
\]  

(S17)

\[
\frac{6 \pi \eta_{\text{solv}}}{k_B T (1 - \bar{c})^2} \lim_{k \to 0} \frac{\Gamma_{\text{fast}}}{k^2} \approx \frac{1 + 2 A_{2, \text{fast}} M_{w, \text{fast}} c}{R_{H, \text{fast}}^\text{app}(c)} \quad \frac{6 \pi \eta_{\text{solv}}}{k_B T} \lim_{k \to 0} \frac{\Gamma_{\text{slow}}}{k^2} \approx \frac{1}{R_{H, \text{slow}}^\text{app}(c)}
\]  

(S18)

where \( M_{w, \alpha} \), \( P_{z, \alpha}(k) \), \( A_{2, \alpha} \), and \( R_{H, \alpha}^\text{app}(c) \) are the weight average molar mass, z-average particle scattering function, the second virial coefficient, and the apparent hydrodynamic radius of the component \( \alpha (= \text{fast, slow}) \), respectively; \( k_B \) is the Boltzmann constant and \( \eta_{\text{solv}} \) is the solvent
viscosity coefficient. The apparent hydrodynamic radii are affected by the inter-particle hydrodynamic interaction as well as by the entanglement, and written in the dilute region as\textsuperscript{8-11}

\[ R_{H,\text{fast}}^{\text{app}} = R_{H,\text{fast}} \left(1 + k_{D,\text{fast}} c\right), \quad R_{H,\text{slow}}^{\text{app}} = R_{H,\text{slow}} \left(1 + k_{D,\text{slow}} c\right) \]  \hspace{1cm} (S19)

where \( k_{D,\text{fast}} \) and \( k_{D,\text{slow}} \) are concentration coefficients with respect to the self-diffusion coefficients of the fast and slow relaxation coefficients, respectively. These interactions in cylindrical micellar solutions are formulated in ref\textsuperscript{8}. Readers should refer to the original paper for these interaction effects on the apparent hydrodynamic radii.

Equation S17 indicates that \( R_{\theta,\text{fast}}/Kc \) is approximately identical with that for the solution without the slow relaxation component given by eq S10, and \( \Gamma_{\text{fast}} \) given by eq S18 is also approximately equal to that for the solution without the slow relaxation component. Thus, we can characterize the fast relation component by combining SLS and DLS, even if the solution contains the slow relaxation component.\textsuperscript{7}

On the other hand, the approximate equations of \( R_{\theta,\text{slow}} \) and \( \Gamma_{\text{slow}} \) in eqs S17 and S18 demonstrate that these experimental quantities for the slow relaxation component provide \( P_{z,\text{slow}}(k) \) and \( R_{H,\text{slow}} \) without extrapolating the quantities to the zero solute concentration, although \( R_{H,\text{slow}} \) is affected by the inter-particle hydrodynamic and entanglement interactions at finite concentrations. In eq S17, \( R_{\theta,\text{slow}} \) is affected by the interaction with the fast relaxation
component, and also contains the unknown weight fraction $w_{\text{slow}}$ (usually a very small number) of the slow relaxation component, although the explicit expression is not given. Therefore, we cannot estimate the aggregation number $m_{w,\text{slow}}$ of the slow relaxation component by SLS and DLS.\(^7\)

**REFERENCES**