LAMBDA DEPRESSION/OVERLAY HISTOGRAM ANALYSIS OF POLY(ACRYLATE) AS A FUNCTION OF ADDED SALT

Kenneth S. Schmitz and Jae-Woong Yu

Department of Chemistry
University of Missouri-Kansas City
Kansas City, Missouri 64110

INTRODUCTION

Dynamic light scattering (DLS) techniques monitor the decay of spontaneous fluctuations in the polarizability of the medium. Any process that results in a change in polarizability can therefore be examined by DLS. The time dependence of these processes can be extracted from the autocorrelation function \([C(t)]\) or spectral density \([S(\omega)]\) of the scattered light. If the light scattered by the supporting medium (solvent and salt) can be neglected, then the molecular (solute) correlation function for the self-beat (homodyne) correlation function can be expressed as,

\[
G(K,t) = \lbrack g_1(K,t) \rbrack^2 + B + \varepsilon(t)
\]

where

\[
g_1(K,t) = \sum_i a_i(K) \exp(-\gamma_i t)
\]

is the molecular correlation function, \(B\) is the baseline, \(\varepsilon(t)\) represents random fluctuating noise, \(a_i(K)\) is the amplitude for the \(i\)th decay process which has a decay rate of \(\gamma_i\), and \(K\) is the scattering vector with magnitude

\[
K = \frac{(4\pi n/\lambda)}{\sin(\theta/2)}
\]

where \(n\) is the index of refraction, \(\lambda\) is the wavelength of the incident light, and \(\theta\) is the scattering angle. The amplitude associated with each decay process is of the general form,

\[
a_i(K) = N'(\delta n / \partial C_i)_{T,\mu}^2 (M_i C_i / N_A) S(Kd_i,Kr_i)
\]

where

\[
N' = \left[ \sum_j (\delta n / \partial C_j)_{T,\mu}^2 (M_j C_j / N_A) S(Kd_j,Kr_j) \right]^{-1}
\]

is the normalization constant, \((\delta n / \partial C_i)_{T,\mu}\) is the index of refraction increment of species \(i\) at constant chemical potential of all other components, \(M_i\) is the molecular weight of component \(i\) at a concentration \(C_i\), \(N_A\) is Avogadro's number, and \(S(Kd_i,Kr_i)\) is the scattering form factor for the \(i\)th component, where \(d_i\) represents the difference in internal coordinates of...
scattering centers located on the ith particle and \( r_{ij} \) is the distance of separation between a scattering center on the ith particle and a scattering center on another particle in the solution. To the first order correction term in the concentration, the structure factor \( S(K_{d_i}, K_{r_i}) \) can be expressed as the sum of "self" and "pair" terms,

\[
S(K_{d_i}, K_{r_i}) = P(K_{d_i}) + \sum_j C_j \left\{ \frac{\langle \partial n/\partial C_j \rangle}{\langle \partial n/\partial C_i \rangle} \right\} T_{i,j} S'(K_{r_j})
\]  

(6)

where the self term is the particle form factor,

\[
P(K_{d_i}) = \frac{1}{n_i} \sum_{i'} \sum_{i''} \exp[iK(d_{i',i''}) - d_{i',i''}]
\]  

(7)

for the \( n_i \) scattering units in the ith polymer, and the pair term,

\[
S'(K_{r_j}) = \langle \sum_{i,j} \frac{1}{n_i n_j} \sum_{i',j'} \exp[iK(r_{cm_{i'}, r_{cm_{j'}}} - r_{cm_{i}, r_{cm_{j}}})] \rangle
\]  

(8)

for the \( N_m \) polymers of type "m" with the center-of-mass located at \( r_{cm_j} \). The general form for the scattering amplitudes \( a_i(K) \) is thus written as,

\[
a_i(K) = M_{i} C_i P(K_{d_i}) \left\{ 1 + \sum_j C_j \left\{ \frac{S'(K_{r_j})}{P(K_{d_j})} \right\} \right\}
\]  

(9)

where the normalization parameter \( N' \) defined by Eq. (5) is omitted for convenience. Clearly, the interpretation of the relative amplitudes as defined by Eq. (9) is somewhat complicated if the relative number density \( C_j \) is desired. For a system containing only one type of particle, the relative amplitude expression takes on the form,

\[
a_i(K) = M_i C_i P(K_{d_i}) \left\{ 1 + \sum_j C_j \left\{ \frac{S'(K_{r_j})}{P(K_{d_j})} \right\} \right\}
\]  

(10)

where the indices \( i \) and \( j \) reflect the polydispersity in molecular weight of the preparation. There are two systems that permit further simplification of Eq. (10): the spherical particle; and the flexible particle with one contact point with other particles.

The Spherical Particle

In the case of the spherical particle the center-of-mass and the internal coordinates can be averaged independently of each other. This is because a rotation about the center-of-mass does not alter the distribution of the internal scattering centers. One can therefore write,

\[
(1/n_i \ n_j) \langle \sum_{i',j'} \exp[iK(r_{i',i'} - r_{j',j'})] \rangle
\]

\[
= \left[ \langle 1/n_i \rangle \langle \exp(iK_{r_{i'}}) \rangle \right] \left[ \langle 1/n_j \rangle \langle \exp(-iK_{r_{j'}}) \rangle \right]
\]

\[
= \left[ P(K_{d_i}) \right]^{1/2} \left[ P(K_{d_j}) \right]^{1/2}
\]

(11)

and

\[
S''(K_{r_{cm_i}}) = \langle 1/n_i \ n_j \rangle \langle \sum_{i,j} \exp[iK(r_{cm_i} - r_{cm_j})] \rangle
\]

(12)

230