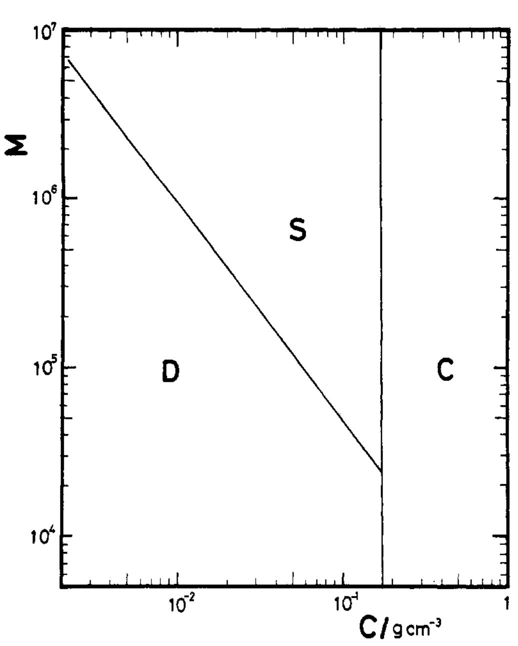

Figure 9. Molecular weight–concentration diagram for polystyrene in toluene or benzene. D, dilute solution; S, semidilute solution; C, concentrated solution.

the entire range of polymer concentration and molecular weight, it is our opinion that we should recognize the existence of the semidilute region to which neither the virial expansion form nor the theory of Flory and Huggins should be applied.

The scaling theory[19] predicts that π/C is proportional to C^2 in concentrated solutions. The experimental data of π/C appear to agree with this prediction in the concentration range 0.3–0.6 g/cm^3 as shown in Figure 3. If we compare the data with the theory of Flory–Huggins, however, we may see that π/C is almost proportional to C^2 in this concentration region owing to the fact that the third term in the expansion form of the equation of Flory and Huggins (eq 6) is relatively large and the second and fourth terms compensate each other though they still contribute to π. In the more concentrated solution the higher terms predominate and the concentration dependence becomes larger as shown in Figure 3.

In sum, we have a molecular weight–concentration diagram for polystyrene in toluene or benzene as shown in Figure 9. The lines dividing the regions do not mean that the thermodynamic properties change discontinuously at the lines but mean that the molecular weight and concentration dependences of the thermodynamic properties of linear polymers solutions are different in these regions.

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Registry No. Polystyrene (homopolymer), 9003-53-6.

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Generalization of the Zimm Equation for Scattering from Concentrated Solutions

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ABSTRACT: The Zimm equation for solution light scattering is normally restricted to dilute solution studies and serves to characterize the solute molecular weight and radius of gyration, and its second virial coefficient describes the solute–solvent interaction. By extending our recent result obtained through use of the Flory–Huggins activity coefficient in the Einstein scattering equations, we show how a modified Zimm equation may be obtained which serves to characterize the Flory interaction parameter χ_{AB} in concentrated solutions. This approach proves useful in the analysis of neutron scattering data from polymer blends.

The Zimm equation[1] is well-known for light scattering measurements of molecular weight in dilute solution. At $q = 0$ [$q = (4\pi/\lambda)\sin(\theta/2)$, where λ is the wavelength of radiation and θ is the scattering angle], this may be written

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as

$$\frac{Kc_{\mathrm{B}}}{R_{\mathrm{c}}(q)} = \frac{1}{M_{\mathrm{B}}} + 2A_2c_{\mathrm{B}} \tag{1}$$

where K is a constant which for light scattering is

$$K_{\mathrm{L}} = \frac{2\pi^2n^2}{N_0\lambda_0^4}\left(\frac{\partial n}{\partial c_{\mathrm{B}}}\right)_{T,p}^2 \tag{2}$$

where n is the refractive index of the solution of concentration c_{B}, N_0 is Avogadro's number, and λ_0 is the wavelength of light in vacuum. $R_{\mathrm{c}}(0)$ is the part of the Rayleigh factor at $q = 0$ arising from concentration fluctuations, which is a measure of the scattering power of the solution and defined as

$$R(q) = \frac{I_{\mathrm{s}}(q)p^2}{I_0V_{\mathrm{s}}} \tag{3}$$

where $I_{\mathrm{s}}(q)$ is the scattering intensity at q, I_0 the incident intensity, p the sample to detector distance, and V_{s} the scattering volume.

M_{B} is the average molecular weight of the solute and A_2 is the second virial coefficient, which is, according to Flory–Huggins (FH) theory,[2]

$$A_2 = \{1/2 - Z_{\mathrm{A}}\chi_{\mathrm{AB}}'\}/\rho_{\mathrm{B}}^2V_{\mathrm{A}} \tag{4}$$

where Z_{A} is the degree of polymerization of the solvent and χ_{AB}' is the interaction parameter between solute and solvent per monomer unit of solvent. (The equation has been generalized to accommodate a polymeric solvent.) ρ_{B} is the density of the solute and V_{A} the molar volume of the solvent. The equation in this form is conventionally used to determine M_{B} as well as χ_{AB}', characterizing the "goodness" of the solvent. Its use is restricted to dilute solution because of the neglect of higher terms in the virial expansion of the chemical potential used in its deviation.

It has been realized that the equation may also be applied to X-ray scattering[3] as well as neutron scattering[4,5] with a redefinition of the constant, K for X-rays as

$$K_{\mathrm{X}} = N_0i_{\mathrm{e}}\left\{\frac{\partial\rho^{\mathrm{e}}}{\partial c_{\mathrm{B}}}\right\}^2 = N_0i_{\mathrm{e}}(\rho_{\mathrm{A}}^{\mathrm{e}} - \rho_{\mathrm{B}}^{\mathrm{e}})^2/\rho_{\mathrm{B}}^2 \tag{5}$$

where i_{e} is the Thomson scattering factor for an electron [$i_{\mathrm{e}} = (e^2/m_{\mathrm{e}}c_0^2)^2$, where e is the electronic charge, m_{e} its mass, and c_0 the velocity of light], ρ^{e}, $\rho_{\mathrm{A}}^{\mathrm{e}}$, and $\rho_{\mathrm{B}}^{\mathrm{e}}$ are the electron densities (moles of electrons/cm^3) of the solution, phases A and B, respectively, and ρ_{B} is the gravimetric density of phase B. For neutrons

$$K_{\mathrm{N}} = (N_0/m_{\mathrm{B}}^2)\left[a_{\mathrm{A}}\frac{V_{\mathrm{B}}}{V_{\mathrm{A}}} - a_{\mathrm{B}}\right]^2 \tag{6}$$

where m_{B} is the molecular weight of the monomer unit of B, a_{A} and a_{B} are the scattering lengths per monomer unit of the two components, and V_{A} and V_{B} are their molar volumes.

It has recently been shown[6] that if Flory–Huggins theory is used for the chemical potential rather than the virial expansion, it is possible to write the scattering equation in the form

$$\frac{K_{\mathrm{B}}m_{\mathrm{B}}^{*2}}{R_{\mathrm{c}}(0)v_0N_0} = \frac{1}{y_{\mathrm{A}}\phi_{\mathrm{A}}} + \frac{1}{y_{\mathrm{B}}\phi_{\mathrm{B}}} - 2\chi_{\mathrm{AB}} \tag{7}$$

The equation here is written in terms of the parameters of a lattice model where m_{B}^* is the mass per mole of lattice cells containing B units. Each lattice cell has a volume v_0, y_{A} and y_{B} are the number of lattice cells occupied by a molecule of A and B, respectively, and ϕ_{A} and ϕ_{B} are the volume fractions of these two components. χ_{AB} is the interaction parameter per lattice cell. The lattice quantities are related to the molecular quantities by

$$m_{\mathrm{B}}^* = m_{\mathrm{B}}(v_0/v_{\mathrm{B}}) \tag{8}$$

$$y_{\mathrm{A}} = Z_{\mathrm{A}}(v_{\mathrm{A}}/v_0) \tag{9}$$

$$y_{\mathrm{B}} = Z_{\mathrm{B}}(v_{\mathrm{B}}/v_0) \tag{10}$$

and

$$\chi_{\mathrm{AB}} = \chi_{\mathrm{AB}}'(v_0/v_{\mathrm{A}}) \tag{11}$$

where v_{A} and v_{B} are the volumes of monomer units of A and B.

It was shown that eq 7 is symmetrical in A and B and that the role of the solute and solvent may be reversed. The subscript B is used in K_{B} to indicate that B is regarded as the solute in these equations where K is defined as in eq 2, 5, and 6. The equation was shown to be a special case of that arising from the de Gennes random-phase approximation.[7] Since, the Flory–Huggins equation is applicable to concentrated solution, eq 7 should not be limited to dilute solution and is, in a sense, a more general form of Zimm's equation.

It should be noted that the value of R_{c} used in eq 7 is only that part arising from concentration fluctuations. The experimental Rayleigh factor is

$$R = R_{\mathrm{c}} + R' \tag{12}$$

where R' is that component of the Rayleigh ratio arising from density fluctuations and incoherent scattering. For dilute solution measurements, it is usually assumed that $R' = R_0$, the scattering by the pure solvent. This is not a good assumption in concentrated solutions. However, it is probably good to assume that both density fluctuations and incoherent scattering vary linearly with volume fraction, so that

$$R' = \phi_{\mathrm{A}}R_{\mathrm{A}} + \phi_{\mathrm{B}}R_{\mathrm{B}} \tag{13}$$

where R_{A} and R_{B} are the total Rayleigh factors for pure A and B. Thus it is necessary to measure these as well as that for the solution.

A better relationship for the density fluctuation contribution to R' is

$$R'_{\mathrm{d}} = [\phi_{\mathrm{A}}(R'_{\mathrm{dA}})^{1/2} + \phi_{\mathrm{B}}(R'_{\mathrm{dB}})^{1/2}] \tag{13a}$$

where R'_{dA} and R'_{dB} are the density fluctuation contributions to the scattering for pure A and pure B. However, since incoherent scattering is the largest contributor to R', eq 13 is a reasonable approximation.

It was pointed out that for light scattering, the result is equivalent to that proposed by Debye and Bueche in 1950.[8] Their concentrated solution result has not been extensively used, however, because of the experimental difficulties of carrying out light scattering in concentrated polymer solutions. An equivalent result has been used for X-ray scattering from polymer blends by Wendorff.[9] We have used this equation for the determination of χ_{AB} by small-angle neutron scattering from polymer blends[10–12] and have obtained values comparable with those obtained by other methods.

Reduction to Zimm Equation

For dilute solution (arbitrarily designating component B as the solute), $\phi_{\mathrm{A}} \approx 1$ and $\phi_{\mathrm{B}} = c_{\mathrm{B}}/\rho_{\mathrm{B}}$, so eq 7 becomes

$$\frac{K_{\mathrm{B}}m_{\mathrm{B}}^{*2}}{R_{\mathrm{c}}(0)v_0N_0} = \frac{1}{y_{\mathrm{A}}} + \frac{\rho_{\mathrm{B}}}{y_{\mathrm{B}}c_{\mathrm{B}}} - 2\chi_{\mathrm{AB}} \tag{14}$$

Then, since $\rho_{\mathrm{B}} = m_{\mathrm{B}}^*/v_0N_0$, $y_{\mathrm{A}} = V_{\mathrm{A}}/N_0v_0$, the equation becomes

$$\frac{K_B c_B}{R_c(0)} = \frac{1}{M_B} + 2\left[\frac{\frac{1}{2} - y_A \chi_{AB}}{V_A \rho_B^2}\right] c_B = \frac{1}{M_B} + 2A_2 c_B \quad (15)$$

which is the conventional Zimm equation for dilute solution. Since eq 7 is symmetrical in A and B, their roles can be reversed, giving

$$\frac{K_A c_A}{R_c(0)} = \frac{1}{M_A} + 2\left[\frac{\frac{1}{2} - y_B \chi_{AB}}{V_B \rho_B^2}\right] c_A \quad (16)$$

It is noted that $\chi_{AB} = \chi_{BA}$.

Generalization of Zimm-Type Equation for Concentrated Solutions

If in eq 7 one lets $\phi_A = 1 - \phi_B = 1 - (c_B/\rho_B)$, then one obtains

$$\frac{K_B m_B{}^{*2}}{R_c(0) v_0 N_0} = \frac{1}{y_A[1 - (c_B/\rho_B)]} + \frac{\rho_B}{y_B c_B} - 2\chi_{AB} \quad (17)$$

which, as before, leads to

$$\frac{K_B c_B}{R_c(0)} = \frac{1}{M_B} + \frac{2}{V_A \rho_B^2}\left[\frac{1}{2[1 - (c_B/\rho_B)]} - y_B \chi_{AB}\right] c_B \quad (18)$$

This may be rearranged to give

$$\left[\frac{K_B}{R_c(0)} - \frac{c_B}{V_A \rho_B^3[1 - (c_B/\rho_B)]}\right] c_B = \frac{1}{M_B} + 2A_2 c_B \quad (19)$$

Thus, by making a modified Zimm plot, subtracting the second term on the left side of the equation from the first, a linear relationship may be obtained from which M_B and χ_{AB} may be obtained from concentrated solution measurements. It is apparent that at sufficiently low concentrations, this extra term is negligible so that the conventional Zimm equation is obtained.

By reversing the role of solvent and solute, eq 19 may be rewritten

$$\left[\frac{K_A}{c(0)} - \frac{c_A}{V_B \rho_A[1 - (c_A/\rho_A)]}\right] c_A = \frac{1}{M_A} + 2(A_2)_A c_A \quad (20)$$

where the subscript A on $(A_2)_A$ indicates that this is a second virial coefficient written with A considered as the solvent, as in eq 14. Thus, by plotting in this form, M_A may be determined. It should be noted that V_A and V_B in eq 19 and 20 are molecular weight dependent. That is, $V_A = v_A Z_A = v_A M_A/m_A$ so the determination of molecular weights requires the simultaneous solution of these equations, possibly using iteration techniques.

It is noted that the $[1 - (c_B/\rho_B)]^{-1}$ term in the denominator of the left side of eq 23 may be expanded in a power series as

$$[1 - (c_B/\rho_B)]^{-1} = 1 + (c_B/\rho_B) + (c_B/\rho_B)^2 + ... \quad (21)$$

so that

$$\frac{K_B c_B}{R_c(0)} =$$

$$\frac{1}{M_B} + 2A_2 c_B + \frac{c_B{}^2}{V_A \rho_A{}^3}[1 + (c_B/\rho_B) + (c_B/\rho_B)^2 + ...]$$

$$= \frac{1}{M_B} + 2A_2 c_B + \frac{c_B{}^2}{V_A \rho_B{}^3} + \frac{c_B{}^4}{V_A \rho_B{}^4} + \frac{c_B{}^5}{V_A \rho_B{}^5} + ...$$

$$= \frac{1}{M_B} + 2A_2 c_B + B_3 c_B{}^2 + B_4 c_4{}^4 + B_5 c_B{}^5 + ... \quad (22)$$

Thus, the Zimm equation for concentrated solutions can be expressed in terms of a virial expansion, where A_2 has its usual form (eq 4) but where the higher virial coefficients are given by

$$B_i = \frac{1}{V_A \rho_B{}^i} \quad (23)$$

The conclusion is that the information about χ_{AB} is entirely included in the second virial coefficient and that the higher virial coefficients, B_i, are independent of interaction.

This result is not surprising in view of the early observations by Huggins[13] that if the FH theory is expanded in terms of virial coefficients, the third (and higher) virial coefficient is independent of χ_{AB}. This result is also pointed out by de Gennes[14] who shows that a low concentration a mean field theory gives this result independently of the assumption of a lattice model.

Huggins, in fact, suggests that one can correct osmotic pressure plots for higher concentration effects by subtraction of a χ_{AB}-independent third virial coefficient from π/c_B, analogous to what we propose for modified Zimm plots in eq 19.

Equation 22 has also been proposed by Hyde[15] who comments on the χ_{AB} independence of the higher virial coefficients. Equivalent developments have been advanced by Scholte.[16] In dilute solution, the deviations from ideality described by the second virial coefficient with increasing concentration contributions from the third and higher virial coefficients represent multiple-contact interactions among molecules and all exhibit characteristic dependencies upon molecular interaction parameters. However, as concentration becomes high, mean field theories (represented by FH theory) become better approximations,[14] in which case, while the high virial coefficients become important, their dependence upon molecular interaction parameters such as χ_{AB} becomes less.

For analysis at other than $q = 0$, eq 7 should be replaced by its equivalent obtained using the result from de Gennes[7]

$$\frac{K_B m_B{}^{*2}}{R_c(q) v_0 N_0} = \frac{1}{y_A \phi_A P_A(q)} + \frac{1}{y_B \phi_B P_B(q)} - 2\chi_{AB} \quad (24)$$

where $P_A(q)$ and $P_B(q)$ are intramolecular interference functions for ideal configurations of the pure phases of A and B, which leads to

$$\left[\frac{K_B}{R_c(q)} - \frac{c_B}{V_A \rho_B{}^3[1 - (c_B/\rho_B)]P_A(q)}\right] c_B =$$

$$\frac{1}{M_B P_B(q)} + 2\left[\frac{\frac{1}{2P_A(q)} - y_A \chi_{AB}}{V_A \rho_B{}^2}\right] c_B \quad (25)$$

For monomeric solvents, $P_A(q)$ is close to unity over the measurable range of q so that (22) reduces to

$$\frac{K_B}{R_c(q)} - \frac{c_B}{V_A \rho_B{}^3[1 - (c_B/\rho_B)]} =$$

$$\frac{1}{M_B P_B(q)} + 2\left[\frac{\frac{1}{2} - y_A \chi_{AB}}{V_A \rho_B{}^2}\right] c_B \quad (26)$$

In this case, a modified Zimm plot permits the measurement of the variation of $P_B(q)$ with q and obtaining the radius of gyration of B.

For polymeric solvents at appreciable concentration, the q variation of scattering depends upon both $P_A(q)$ and $P_B(q)$ in a fairly complex way, so that the resolution of the data to obtain radii of gyration of both species A and B is not apparent. In this case, it is better to use the three-component technique previously discussed[10-12] to obtain radii of gyration.

We have found along with others, that χ_{AB} for polymer blends is often concentration dependent. This is a consequence of the inadequacy of the constant-volume lattice model on which the FH theory is based. Modified theories such as Sanchez's lattice theory[17] and equation of state theories[18,19] may be employed[20] to better describe scattering in terms of parameters having more molecular significance. In this case, in the deviation of eq 7,[6] where the derivative of osmotic pressure with respect to concentration $(\partial\pi_A/\partial c_B)$ is taken, the derivative $(\partial\chi_{AB}/\partial c_B)$ would be finite and should be included. Since this is not known, a priori a suggested procedure is to iterate by calculating χ_{AB} at various concentrations using the procedures suggested in this paper, then represent χ_{AB} as an empirical function of concentration, say

$$\chi_{AB} = (\chi_{AB})_0 + (\chi_{AB})_1 c_B + (\chi_{AB})_2 c_B^2 + ... \qquad (27)$$

and rederive eq 7 taking this variation into account. Unless the concentration variation of χ_{AB} is large, it is not expected that this correction will be large.

A more correct theory would replace the χ_{AB} values of the FH with equivalent values which are truly enthalpic and would be concentration independent. In that case, the higher virial coefficients would generally depend upon interaction parameters.

It is reasonable that the FH theory result is consistent with the de Gennes result in both the concentrated and semidilute regime for polymeric solvents where the mean field theory approach is applicable. It is somewhat surprising that the results correspond in the semidilute regime for low molecular weight solvents where scaling theory, following the des Cloizeaux law, should be more appropriate than the FH theory.

Conclusions

A modified Zimm analysis of scattering data may be applied to concentrated as well as dilute binary solutions. For polymeric solvents, the molecular weight and interaction parameter may be obtained from such analysis. For monomeric solvents, the radius of gyration of the solute may also be obtained.

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