

INTERPRETATION OF PREFERENTIAL ADSORPTION USING RANDOM PHASE APPROXIMATION THEORY

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Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.

It has been shown that in light scattering experiments with polymers replacement of a solvent by a solvent mixture causes problems due to preferential adsorption of one of the solvents. The present paper extends this theory to be applicable to any angle of observation and any concentration by using the random phase approximation theory proposed by de Gennes. The corresponding formulas provide expressions for molecular weight, gyration radius, and the second virial coefficient, which enables measurements of these quantities provided enough information on molecular and thermodynamic quantities is available.

A few decades ago, research in the field of light scattering was focused to the interpretation of results of light scattering in ternary systems such as that of one polymer dissolved in a mixture of two solvents. It was recognized by Ewart, Roe, Debye, and MacCartney¹ that application of a solvent mixture instead of a pure liquid resulted in an incorrect value of the molecular weight of the polymer under study. This discrepancy is of practical importance since determination of molecular weights of exotic polymers insoluble in pure solvents necessitates solvent mixtures or solvents with an additional third component. This is the case, e.g., with poly-benzyl glutamate where hydrogen bond breakers must be added to ensure solubility, and polyelectrolytes which are always dissolved in the presence of a buffer. An explanation based on the concept of preferential sorption was proposed by Debye¹ and studied carefully by many experimentalists. The experimental results can be interpreted by using the theory of scattering by multicomponent systems established by Stockmayer², Kirkwood and

* The Editorial Board announces with regret that Dr Claude Strazielle passed away on 10th September 1995. His decease is a great loss for polymer science, particularly for people working in the field of light scattering to which he contributed by significant findings.

Goldberg³ and adapted for mixed solvents by Read⁴. So far the problem has been limited to the zero-angle scattering and infinitely diluted solutions, which is thermodynamically simple and useful for molecular weight determination. The results were expressed in terms of the Flory⁵ and Huggins⁶ theory of the free energy of mixing.

The aim of the present paper is to extend these results to any concentration of the constituents and any angle of observation using the Random Phase Approximation theory developed by de Gennes⁷.

THEORETICAL

Thermodynamical Aspect of Problem of Scattering by Polymer Mixtures

Following Flory and Huggins⁵, let us use a lattice model. This is an artifice to describe the phenomena, but it does not limit the validity of the results. Each site of the lattice has a volume v_0 equal to the volume of a solvent molecule. The polymer molecule of species i occupies z_i sites; hence it has the volume $v_i = z_i v_0$. Denoting the total number of cells of the lattice as N_T , that of solvent molecules as N_0 , and that of molecules of species i (where i varies from 1 to p) as N_i , and the volume fraction occupied by species i as φ_i ($\varphi_i = z_i N_i / N_T$), we get

$$N_T = N_0 + \sum_{i=1}^p z_i N_i \quad (1)$$

and

$$\varphi_0 + \sum_{i=1}^p \varphi_i = 1 .$$

For the scattering volume to equal unity it is sufficient to define N_T as v_0^{-1} , which gives $N_T v_0 = 1$.

It is known⁸ that the intensity I scattered by an incompressible medium formed by p different polymer types is expressed by the simple formula:

$$I = C \sum_{i=1}^p \sum_{j=1}^p (a_i - a_0)(a_j - a_0) S_{ij}(0) , \quad (2)$$

where C is a constant, and $S_{ij}(0)$ is the value of expression (3) extrapolated to $q = |\mathbf{q}| = 0$.

$$S_{ij} = \frac{1}{N_T} \left\langle \sum_{k=1}^{z_i} \sum_{l=1}^{z_j} \exp -iq \cdot (r_{ki} - r_{lj}) \right\rangle . \quad (3)$$

The index zero refers to what is considered the solvent and the indexes i ($1 \leq i \leq p$) refer to the individual p species (different from solvent) present in the solution. The S_{ij} 's are called the partial structure factors relative to species i and j and are normalized to be intensive quantities. The a_i values are polarizabilities of the individual species i that are related to the increment of refractive index ($dn/d\varphi_i$) which is the derivative of refractive index of the solution with respect to the volume concentration φ_i of the constituent i (the volume concentrations are used here instead of weight concentrations to obtain simpler calculation). Using these notation we get:

$$a_i - a_0 \approx 2n_0(\partial n/\partial\varphi_i)v_0 , \quad (4)$$

where n_0 is the refractive index of solvent.

Owing to the symmetry of problem, $S_{ij}(q) = S_{ji}(q)$, the number of unknown functions is $(1/2)p(p + 1)$ since the incompressibility hypothesis allows elimination of the partial structure factors concerning the solvent. Application of the classical theory of scattering leads to Eq. (5) or (6) for the Rayleigh⁹ constant R of the system (the ratio of the intensity scattered by the unit volume to the incident energy entering this volume):

$$R = \frac{4\pi^2}{\lambda_0^4} n_0^2 v_0 \sum_{i=1}^p \sum_{j=1}^p \frac{\partial n}{\partial\varphi_i} \frac{\partial n}{\partial\varphi_j} S_{ij} \quad (5)$$

or

$$R = \frac{K}{N_T} \sum_{i=1}^p \sum_{j=1}^p v_i v_j S_{ij} \quad (6)$$

with $K = 4\pi^2 n_0^2 / \lambda_0^4$ and $v_i = \partial n / \partial\varphi_i$.

In these formulas, λ_0 is the wavelength of the incident beam in vacuum and n_0 is refractive index of the system. Equations (5) or (6) offer the use of a matrix for S_{ij} which will be denoted as $[S_{ij}]$ (ref.¹⁰). For zero angle, thermodynamics provides the following expression:

$$[S_{ij}(q=0)] = k_B T \left[\frac{\partial^2 g_c}{\partial\varphi_i \partial\varphi_j} \right]^{-1} , \quad (7)$$

where g_c is the free enthalpy per cell or per volume of one solvent molecule, k_B is the Boltzmann constant, and T stands for the absolute temperature. The superscript -1 indicates the inverse of the matrix.

Let us introduce the excluded volume parameters v_{ij} (ref.¹¹) defined as:

$$v_{ij} = \frac{1}{v_0} \int_0^{\infty} \{1 - \exp[-U_{ij}(r)/k_B T]\} 4\pi r^2 dr, \quad (8)$$

where U_{ij} means the average interaction energy between units of type i and j at the distance r in the actual solution. Hence

$$\frac{1}{k_B T} = \frac{\partial^2 g_c}{\partial \phi_i \partial \phi_k} = v_{ik}, \quad (9)$$

$$\frac{1}{k_B T} \frac{\partial^2 g_c}{\partial \phi_i^2} = \frac{1}{z_i \phi_i} + v_{ii}. \quad (10)$$

Introducing Eqs (9) and (10) into Eq. (7) gives¹⁰:

$$[S_{ij}]^{-1} = \begin{pmatrix} \frac{1}{z_1 \phi_1} + v_{11} & v_{12} & \dots & v_{1p} \\ v_{21} & \frac{1}{z_2 \phi_2} + v_{22} & \dots & v_{2p} \\ \dots & \dots & \dots & \dots \\ v_{p1} & v_{p2} & \dots & \frac{1}{z_p \phi_p} + v_{pp} \end{pmatrix}. \quad (11)$$

The excluded volume parameters being known, the only problem is evaluation of S_{ij} , i.e. of the inverse of matrix. As long as the number of constituents is low, this presents no problem. For application of the Flory-Huggins theory it is sufficient to replace v_{ij} by χ_{ij} values using the relations:

$$v_i = v_{i0} = \phi_0^{-1} - 2\chi_{i0} \quad \text{and} \quad v_{ik} = v_{ki} = \phi_0^{-1} + \chi_{ik} - \chi_{i0} - \chi_{k0}. \quad (12)$$

Random Phase Approximation

The theory summarized in Eq. (11) is rigorous and shows that the determination of the zero angle scattering requires the knowledge of the second derivatives of the free enthalpy

of system. It is important to extend this theory to the scattering at any angle, i.e., at any scattering vector \mathbf{q} , $|\mathbf{q}| = q = (4\pi/\lambda) \sin(\theta/2)$ (where λ is wavelength of the scattered light in the medium and θ is the observation angle). The problem was solved in 1972 by de Gennes^{7,12}, who developed the so-called "Random Phase Approximation" (R.P.A.). We are not going to derive the respective formula, and we will give the results without proof.

For introducing the q dependence let us introduce the form factors $P_i(q)$ of each species present in the scattering medium (except for the solvent, which is considered a small molecule): the form factor is defined by Eq. (13):

$$g_i(q) = z_i P_i(q) = \frac{1}{z_i} \sum_{k=1}^{z_i} \sum_{l=1}^{z_i} \langle \exp -i\mathbf{q} \cdot \mathbf{r}_{kl} \rangle . \quad (13)$$

These equations have been normalized in order to have $P(0) = 1$, or $g(0) = z_i$.

Replacing each term $\varphi_i z_i$ by $\varphi_i g_i(q)$ gives the R.P.A. equation for multicomponent media, which represents a useful approximation although it neglects the concentration fluctuations. This remark is not intended to justify the result; it is just a short way to write the scattering equation without any proof.

Let us now write explicitly the formulas valid for systems of two components (polymer and solvent) and three components (two polymers and solvent). In the former case (a and 0 for polymer and solvent, respectively) it is:

$$R^{-1} = \frac{1}{Kv_a^2} \left[\frac{1}{\varphi_a g_a(q)} + v_{aa} \right] \quad (14a)$$

and, within the framework of the Flory theory,

$$R^{-1} = \frac{1}{Kv_a^2} \left[\frac{1}{\varphi_a g_a(q)} + \frac{1}{\varphi_0} - 2\chi_{a0} \right] . \quad (14b)$$

In the latter case with two polymers (a and b) and solvent (0), we shall first simplify the expressions as follows:

$$x_a = \varphi_a g_a(q) , \quad x_b = \varphi_b g_b(q) . \quad (15)$$

Adopting Eq. (11) will give the well-known expression (16) for the Rayleigh factor

$$R = K \frac{v_a^2 x_a + v_b^2 x_b + x_a x_b [v_a^2 v_b + v_b^2 v_a - 2v_a v_b v_{ab}]}{1 + v_a x_a + v_b x_b + (v_a v_b - v_{ab}^2) x_a x_b} \quad (16)$$

These formulas are written in terms of $z_i = v_i/v_0$ and volume fractions φ_i . For expressing the concentrations in mass per unit volume we have to introduce the specific mass ρ_i ($c_i = \rho_i \varphi_i$), replace v_i by $\partial n / \partial c_i = v_i / \rho_i$, and introduce the molecular weight $M_i = \rho_i z_i N_A / N_T$ where N_A is the Avogadro number.

Problem of Preferential Adsorption

When treating a mixture of solvent 0 and polymer b as a single component, we have to subtract the scattering by the solvent mixture from that of the solution. This scattering can be obtained assuming that $\varphi_a = 0$ and keeping φ_b and φ_0 constant. The resulting intensity is denoted as $R'_{b,0}$ since it is not – strictly speaking – a Rayleigh factor.

$$R'_{b,0} = K \frac{v_b^2 \varphi_b g_b(q)}{1 + v_b \varphi_b g_b(q)} = K \frac{v_b^2 x_b}{1 + v_b x_b} \quad (17)$$

with

$$\Delta R = R_{a,b,0} - R'_{b,0} \quad (18)$$

or

$$\Delta R = K x_a \left[v_{a0} - v_{b0} \frac{x_b v_{ab}}{1 + v_b x_b} \right]^2 \left[\frac{1 + v_b x_b}{1 + v_a x_a + v_b x_b + (v_a v_b - v_{ab}^2) x_a x_b} \right] \quad (19)$$

NB: It was possible to use $R_{b,0}$ (which is equal to $R'_{b,0}/(1 - \varphi_a)$) instead of $R'_{b,0}$ which is usually done for binary mixtures by writing Eq. (20) instead of Eq. (18):

$$\Delta R = R_{a,b,0} - R'_{b,0}/(1 - \varphi_a) \quad (20)$$

At low φ_a values both the equations give the same result, the difference between them becoming important only at high φ_a values, a region to be discussed later in this article. The main advantage of Eq. (19) is its form of the product of two expressions, one of them being a perfect square and easier to handle.

In the following, Eq. (19) will be used considering the mixture of polymer b and solvent 0 as a new solvent (called s) and new quantities will be introduced, viz. $\varphi_s = \varphi_0 + \varphi_b$ (the volume fraction of the mixed solvent) and $u = \varphi_b/\varphi_s$ (which defines the volume fraction of polymer b in solvent s).

Preferential Adsorption Coefficient

If the system behaves as a two-component system, Eq. (19) can be written using only the refractive index increment v_{as} between the polymer a and the solvent s (solution of species b in solvent 0) defined as $v_{as} = v_{a0} - uv_b$. At low concentrations it is:

$$\Delta R = K\varphi_a z_a P_a(q) v_{as}^2 (1 + \varphi_a \dots) \quad (21)$$

In fact, introducing v_{as} changes Eq. (19) to the form (22) valid for any concentration,

$$\Delta R(q=0) = Kx_a \left[v_{as} - v_{b0} - \frac{x_b v_{ab} - u(1 + v_b x_b)}{1 + v_b x_b} \right]^2 \left[\frac{1 + v_b x_b}{1 + v_a x_a + v_b x_b + (v_a v_b - v_{ab}^2) x_a x_b} \right] \quad (22)$$

which could be written as

$$\Delta R = Kx_a [v_{as} - v_{b0} \Lambda]^2 \left[1 + x_a \left(v_a - \frac{v_{ab}^2 x_b}{1 + v_b x_b} \right) \right]^{-1} \quad (23)$$

with

$$\Lambda = \frac{x_b v_{ab} - u(1 + v_b x_b)}{1 + v_b x_b} \quad (24)$$

Λ is the coefficient of preferential solvation; it can be evaluated either by thermodynamic arguments (as shown by Casassa and Eisenberg¹³⁻¹⁵) or by geometrical arguments¹⁶ at the limit of $\varphi_a = 0$.

Another way of introducing the differences between systems formed by two and three components is Eq. (25) (as in the case of a simple solvent):

$$\Delta R = K\varphi_a z_{app} \{v_{as}\}^2 \{1 + \varphi_a \dots\}^{-1} \quad (25)$$

This introduces an apparent molecular weight z_{app} for the constituent a, which would be obtained if the systems were not considered a three-component one. The relation between Λ and z_{app} following from Eqs (23)–(25) reads as follows:

$$\Lambda = \frac{v_{\text{as}}}{v_{\text{b0}}} \left[\sqrt{\frac{z_{\text{app}}}{z_a}} - 1 \right] = \frac{x_b v_{\text{ab}} - u(1 + v_b x_b)}{1 + v_b x_b} \quad (26)$$

It is interesting to express Λ in terms of Flory's theory; assuming $q = 0$, this will lead to:

$$\Lambda = \frac{\varphi_b}{\varphi_0 + \varphi_b} \frac{z_b - 1 + z_b(\chi_{\text{ab}} - \chi_{\text{b0}} - \chi_{\text{a0}})(\varphi_0 + \varphi_b) + 2\chi_{\text{b0}}z_b\varphi_b}{1 + z_b \frac{\varphi_b}{\varphi_0} - 2\chi_{\text{b0}}z_b\varphi_b} \quad (27)$$

Replacing z_b by $g_b(q)$ in order to visualize the q dependence of scattering leads to

$$\Lambda = \varphi_0 \varphi_b \left\{ \frac{\left[\frac{[g_b(q) - 1]}{\varphi_0 + \varphi_b} + g_b(q) \left[\chi_{\text{ab}} - \chi_{\text{a0}} - \chi_{\text{b0}} \frac{\varphi_0 - \varphi_b}{\varphi_0 + \varphi_b} \right] \right]}{\varphi_0 + \varphi_b g_b(q) (1 - 2\chi_{\text{b0}}\varphi_0)} \right\} \quad (28)$$

or rewritten in terms of u and φ_a :

$$\Lambda = u(1 - u) \frac{g_b(q) - 1 + (1 - \varphi_a)g_b(q)[\chi_{\text{ab}} - \chi_{\text{a0}} - \chi_{\text{b0}}(1 - 2u)]}{1 - u + u g_b(q)(1 - 2\chi_{\text{b0}}(1 - u)(1 - \varphi_a))} \quad (29)$$

For low φ_a values (dilute solution) the term $(\varphi_0 + \varphi_b = 1 - \varphi_a)$ can be replaced by unity, which reduces (after extrapolation to $q = 0$) Eq. (29) to the result obtained by Read⁴ by application of the Stockmayer² theory of scattering in multicomponent mixtures. (There is a small difference in the form of the results which is due to the differences in the definitions of the interaction parameters.)

Hence, the scattering by a ternary system can be transformed into the same mathematical form as that by a binary mixture: the system is considered as one polymer dissolved in a mixture formed by the other two components. An artificial refractive index difference is introduced through the definition of Λ . It depends on thermodynamical and optical parameters, and if the Λ parameter is adjusted as a function of concentration, the result is valid for any composition of the system.

It was shown^{13,14} that at low concentrations the value of $v_{\text{as}} - \Lambda v_{\text{b0}}$ is directly obtained if the solvent used for measuring v is in thermodynamical equilibrium (e.g., through a semipermeable membrane) with the solution. This result was explained by assuming that the composition of the solvent inside the coil is different from that far

away from it. Hence for the refractive index difference it is necessary to adopt the refractive index of the dissolved molecule increased by that of the solvent adsorbed in its vicinity. This explanation is quite successful for small ϕ_a values but fails in the case of solutions with concentrations above the critical concentration of overlapping ϕ_a^* since in this concentration range it is impossible to differentiate between the inside and the outside of a dissolved molecule. Nevertheless, the same mathematical form for the scattering intensity can be used at any concentration.

The result just shown can be considered an alternative presentation of the Random Phase Approximation and is subject to the same limitations since it (as a mean field approximation) fails when fluctuations are important.

It should be noted that the polarizability of the various constituents of a mixture is more complex than the scattering length in the case of neutrons. This means that the approximation used (which linearizes the relation between polarizability and refractive index) can sometimes be too crude; in such cases the formulas should be modified to remain correct.

DISCUSSION

What Affects the Value of Λ Parameter?

When does the preferential adsorption disappear? The first interesting problem is to find the conditions which must be fulfilled in order to suppress the preferential adsorption or to make $\Lambda = 0$. Equation (27) shows that three conditions must be fulfilled simultaneously: (i) $z_b = 1$ (the solvents 0 and b have the same molar volume), (ii) $\chi_{a0} = \chi_{ab}$ (the interaction of the polymer a with solvent b is the same as that of a with 0), and (iii) $\chi_{b0} = 0$ (the solvents are thermodynamically identical). If they are fulfilled, the behaviour is normal and the solvent mixture can be treated as a single solvent.

Effect of molecular weight of polymer a. Equation (29) suggests that Λ is independent of molecular weight. This was verified by Strazielle¹⁶ using the system of polystyrene dissolved in benzene–cyclohexane mixture, but the law is not general, and there are cases when it is violated (Dondos and Benoît¹⁷, Hert et al.¹⁸).

Effect of solvent composition. At low ϕ_a values the Λ factor is the product of $\phi_0\phi_b \approx u(1-u)$ by a slowly varying term independent of the polymer a. For $0 \leq u \leq 1$ the plot of Λ against u resembles parabola ($\Lambda = 0$ for $\phi_0 = 0$ or $\phi_b = 0$). This type of behaviour was observed by Read⁴ and Strazielle and Benoît¹⁶ in a polystyrene–benzene–cyclohexane system, but it is rarely measured since it is common to use the precipitant of polymer a for the solvent b.

Effect of z_b . At very high z_b values, if the solvents are identical except for the size, it is $\Lambda = 1 - u$, which means that the refractive index increment to be used is $v_{a0} - v_{b0}$ instead of $v_{a0} - uv_{b0}$ (i.e., for large z_b values the scattering of b is so large that that of the solvent 0 can be neglected).

Effect of Concentration, Size Difference, and Quality of Solvent on Λ and on Scattered Intensity

Equations (19), (20), and (22) allow a qualitative discussion of the scattering aspects that can be observed in various experimental situations.

Effect of solvent quality. It is known that the scattered intensity increases to infinity at the spinodal (Eq. (30a) or (30b)).

$$1 + v_{b0}x_b = 0 \quad (30a)$$

$$1 + v_{a0}x_a + v_{b0}x_b + (v_{a0}v_{b0} - v_{ab}^2)x_ax_b = 0 \quad (30b)$$

This does not mean that the system has two spinodals but only reflects the fact that Eq. (23) summarizes the result of two scattering experiments, one for "solvent" and the other for "solution"; in both cases one has to work in a single phase mixture. It also would be appropriate to discuss the effect of solvent quality considering the values of v_a , v_b , and v_{ab} parameters or those of Flory's χ_{a0} , χ_{b0} , and χ_{ab} parameters. Such discussion must be delayed until these formulas can be compared with experimental data.

Radius of Gyration and Second Virial Coefficient

Radius of Gyration

It is known that, for polymer solutions, the inverse representation, $R^{-1}(q)$ as a function of concentration, is often more convenient. If used for Eq. (23), it gives

$$\frac{K}{\Delta R(q)} = \frac{1}{\{v_{as} - v_{b0}\Lambda\}^2} \left\{ \frac{1}{x_a} + \frac{v_a + (v_av_b - v_{ab}^2)x_b}{1 + v_bx_b} \right\} \quad (31)$$

Since x_a is equal to $\phi_a z_a P(q)$, this equation has exactly the same form as the corresponding equation for a binary mixture. It allows us to define an apparent radius of gyration and a second virial coefficient. As for the radius of gyration, it can be seen that when neglecting the dependence of Λ on q (assuming that the polymer b is of low molecular weight), the apparent radius of gyration is equal to the real radius of gyration which is measured in one solvent as long as the solvent b has negligible dimensions compared to the wavelength of the incident light. If this is not the case, the Λ parameter will depend on q and introduce changes in \bar{R}^2 - value of the radius of gyration of the polymer a around its centre of mass⁸. This effect will probably be small. This disagrees with Yamakawa's

results^{19,20} and is probably due to the fact that we use Eq. (18), subtracting $R_{b,0}(q)$ rather than $R'_{b,0}(q)$. Another interesting point is the behaviour at large q values. In this case, the arguments developed in ref.²¹ show that the scattering curve is independent of the interactions. The calculation for a Gaussian chain will give Eq. (32) for x_a at high q

$$\frac{1}{x_a} = \frac{1}{\phi_a} \left(\frac{q^2 a^2}{12} + \frac{1}{2z_a} \right), \quad (32)$$

where a is the length of statistical element. Using this value and a similar value for the polymer b we obtain Eq. (33) at high q values

$$\frac{K}{\Delta R(q)} \approx \frac{1}{(v_{as} - v_{b0}\Lambda)^2} \frac{1}{\phi_a} \frac{q^2 a^2}{12}. \quad (33)$$

The polymer b does not appear since its contribution has been suppressed by the subtraction of the solvent. The result is similar to that for a simple solvent, the only difference being the necessity to adopt, as in the case of low angle scattering, the apparent refractive index increment which depends on Λ .

Second Virial Coefficient

The case of the second virial coefficient is also very simple: relation (34) is obtained from Eq. (23) if the Λ term is independent of concentration; but Eq. (29) shows that this is generally not true.

$$(A_2)_{\text{app}} = (A_2)_{a0} - \frac{2(A_2)_{ab}^2 c_b M_b}{1 + 2(A_2)_{b0} c_b M_b} \quad (34)$$

Equation (34) could be corrected, which, however, leads to a long expression which is only useful in cases related to experimental results. From Eq. (29) it can be seen that for A_{2b0} positive and large the effect of the denominator becomes important: it makes the mixture a less good solvent than the pure solvent 0 for polymer a. The apparent value $(A_2)_{\text{app}}$ can also depend on q when $P_b(q)$ decreases below unity; it introduces an increase in $(A_2)_{\text{app}}$ especially in the cases of good solvents when the numerical coefficient in the denominator is larger than that in the numerator.

CONCLUSION

The paper shows that the use of the "Random Phase Approximation" completes and substantially improves the results obtained earlier; it should be used for careful studies of ternary systems. It would have been interesting to show with various examples the consequences of these formulas on the interpretation experiments, but the number of parameters is too large to make a systematic inventory of the various cases; this work will be done in subsequent papers when presenting experimental results.

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